Diquat Derivatives: Highly Active, Two-Dimensional Nonlinear Optical Chromophores with Potential Redox-Switchability

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Supporting Information

1. Experimental Details

Materials and Procedures. Dichloromethane and acetonitrile were dried over CaH_2 and distilled under argon. All other reagents and solvents were obtained as ACS grade from Sigma Aldrich, Alfa Aesar or Fisher Scientific and used as supplied. The compounds 4-[(*E*)-4-(4-dimethylaminophenyl)buta-1,3-dienyl]-4′-methyl-2,2′-bipyridyl (**1**),[1] 2,11-dimethyl-6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinium dibromide ([Me_2EDQ^{2+}]Br_2),[2] 2,12-dimethyl-7,8-dihydro-6*H*-dipyrido[1,2-*a*:2′,1′-*c*]-[1,4]diazepinium dibromide ([Me_2PDQ^{2+}]Br_2),[2] 4,4′-bis-[(diethoxyphosphinyl)methyl]-2,2′-bipyridyl,[3] 1,3-bis(triflyloxy)propane,[4] 2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline-9-carbaldehyde (Jdca)[5] and (*E*)-3-(2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)propenal (Jdpa)[5b] were synthesized by following previously published methods. Products were dried at room temperature overnight in a vacuum desiccator ($CaSO_4$) prior to characterization.

General Physical Measurements. ^{1}H NMR spectra were recorded on Bruker UltraShield 500, AV-400, DPX-300 or Varian Gemini 200 spectrometers and all shifts are quoted with respect to TMS. The fine splitting of pyridyl or phenyl ring AA′BB′ patterns is ignored and the signals are reported as simple doublets, with *J* values referring to the two most intense peaks. Abbreviations: ax = axial; eq = equatorial. Elemental analyses were performed by the Microanalytical Laboratory, University of Manchester using a Carlo Erba EA1108 instrument, and thermogravimetric analyses were also obtained in this Laboratory. UV–vis spectra were obtained by using a Shimadzu UV-2401 PC spectrophotometer, and mass spectra were recorded by using +electrospray on a Micromass Platform II spectrometer. Cyclic voltammetric measurements were performed by using an EG&G PAR model 283 or an Autolab PGStat 100 potentiostat/galvanostat. A single-compartment cell was used with a silver/silver chloride reference electrode (3 M NaCl, saturated AgCl) separated by a salt bridge from a 2 mm disk glassy carbon working electrode and Pt wire auxiliary electrode. Acetonitrile was freshly distilled (from CaH_2) and [$N(C_4H_9$-*n*$)_4$]PF_6, as supplied from Fluka, was used as the supporting electrolyte. Solutions containing ca. 10^{-3} M analyte (0.1 M electrolyte) were deaerated by purging with N_2. All $E_{1/2}$ values were calculated from (E_{pa} + E_{pc})/2 at a scan rate of 200 mV s^{-1}.

Synthesis of 4,4′-Bis[(*E*)-4-(4-dimethylaminophenyl)buta-1,3-dienyl]-2,2′-bipyridyl, 2. Potassium *tert*-butoxide (312 mg, 2.78 mmol) was added to a solution of 4,4′-bis-[(diethoxyphosphinyl)methyl]-2,2′-bipyridyl (500 mg, 1.10 mmol) and (*E*)-4-(dimethylamino)cinnamaldehyde (384 mg, 2.19 mmol) stirred in tetrahydrofuran (20 mL), resulting in near instantaneous production of a yellow precipitate. After stirring at 50 °C for 16 h, water (20 mL) was added and the tetrahydrofuran removed in vacuo. The yellow product was filtered off, washed with cold water then a small amount of methanol and dried: 492 mg, 87%; δ_H (500 MHz, CD_3CN + CF_3CO_2D) 8.63 (2 H, d, *J* = 5.7 Hz, C_5H_3N), 8.50 (2 H, s, C_5H_3N), 7.78 (2 H, d, *J* = 6.0 Hz, C_5H_3N), 7.70–7.64 (6 H, C_6H_4 + 2CH), 7.35 (4 H, d, *J* = 8.8 Hz, C_6H_4), 7.22–7.16 (2 H, m, 2CH), 7.03 (2 H, d, *J* = 15.5 Hz, 2CH), 6.86 (2 H, d, *J* =

15.5 Hz, 2CH). Anal. Calcd (%) for $C_{34}H_{34}N_4 \bullet H_2O$; C, 79.04; H, 7.02; N, 10.84. Found: C, 79.22; H, 6.81; N, 10.69.

Synthesis of Tetra-*n*-butylammonium 2-Naphthalenesulfonate, [N(C_4H_9-*n*)$_4$]NapSO$_3$. Tetra-*n*-butylammonium hydroxide (40% aqueous, ca. 5 mL) was added to a solution of naphthalenesulfonic acid (1.60 g, 7.68 mmol) in water/methanol (1:1, 20 mL) until the pH reached 7. The resulting solution was evaporated to dryness and the residue dried under vacuum. This off-white solid was dissolved in acetone (20 mL) and diethyl ether was added until the solution became turbid. After cooling in a refrigerator, the colorless, crystalline solid was filtered off, washed with diethyl ether and dried: 3.03 g, 88%; δ_H (400 MHz, $(CD_3)_2CO$) 8.28 (1 H, s, Nap), 7.94–7.84 (3 H, m, Nap), 7.80 (1 H, d, J = 8.6 Hz, Nap), 7.51–7.44 (2 H, m, Nap), 3.44–3.38 (8 H, m, $4NCH_2$), 1.81–1.71 (8 H, m, $4CH_2$), 1.38 (8 H, m, J = 7.6 Hz, $4CH_2$), 0.94 (12 H, t, J = 7.3 Hz, 4Me). Anal. Calcd (%) for $C_{26}H_{43}NSO_3$: C, 69.44; H, 9.64; N, 3.11; S, 7.13. Found: C, 69.00; H, 9.94; N, 3.11; S, 7.16.

Synthesis of 2-Methyl-11-[(*E*)-2-(4-dimethylaminophenyl)ethenyl]-6,7-dihydro-dipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium Hexafluorophosphate, [3][PF$_6$]$_2$. A solution of [EDQ^{2+}]Br$_2$ (100 mg, 0.269 mmol), 4-(dimethylamino)benzaldehyde (40 mg, 0.268 mmol) and pyridine (2 drops) in methanol (20 mL) was heated at reflux for 22 h. The solution was cooled to room temperature, added dropwise to diethyl ether (400 mL) and the resulting blue precipitate filtered off. This crude dibromide product was dissolved in methanol and addition of aqueous NH_4PF_6 afforded a dark purple precipitate. The suspension was reduced in volume under vacuum and the precipitate filtered off, washed with methanol and dried. Further purification was achieved by reprecipitation from acetonitrile/diethyl ether to afford a dark purple solid: 43 mg, 25%; δ_H (500 MHz, CD_3CN) 8.70 (1 H, d, J = 6.6 Hz, C_5H_3N), 8.68 (1 H, s, C_5H_3N), 8.58 (1 H, s, C_5H_3N), 8.43 (1 H, d, J = 6.6 Hz, C_5H_3N), 8.07–8.01 (2 H, C_5H_3N + CH), 7.90 (1 H, d, J = 6.8 Hz, C_5H_3N), 7.66 (2 H, d, J = 9.1 Hz, C_6H_4), 7.15 (1 H, d, J = 15.8 Hz, CH), 6.83 (2 H, d, J = 8.8 Hz, C_6H_4), 4.98–4.93 (2 H, m, CH_2), 4.84–4.80 (2 H, m, CH_2), 3.10 (6 H, s, NMe_2), 2.80 (3 H, s, Me). Anal. Calcd (%) for $C_{23}H_{25}F_{12}N_3P_2 \bullet H_2O$: C, 42.41; H, 4.18; N, 6.45. Found: C, 42.68; H, 3.90; N, 6.42. *m/z* = 488.9 ([M – PF$_6$]$^+$), 171.7 ([M – 2PF$_6$]$^{2+}$).

Synthesis of 2-Methyl-11-[(*E*)-4-(4-dimethylaminophenyl)buta-1,3-dienyl]-6,7-dihydro-dipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium Hexafluorophosphate, [4][PF$_6$]$_2$. This compound was prepared in manner similar to [**3**][PF$_6$]$_2$ by using (*E*)-4-(dimethylamino)cinnamaldehyde (47 mg, 0.268 mmol) in place of 4-(dimethylamino)benzaldehyde and pyridine (3 drops) in argon-degassed methanol (50 mL) with a reaction time of 20 h. The resulting deep purple solution was reduced in volume to ca. 20 mL under vacuum, cooled to room temperature, and the crude dibromide salt precipitated by addition to diethyl ether (200 mL) and filtered off. Purification was effected by column chromatography on silica gel, eluting with a gradient of 35:4:1 to 16:2:1 acetone/water/saturated aqueous KNO_3. The major purple band was collected and addition of aqueous NH_4PF_6 afforded a precipitate which was filtered off, washed with water and dried. Further purification was achieved by reprecipitation from acetonitrile/diethyl ether to give a

dark purple solid: 36 mg, 20%; δ_H (400 MHz, CD_3CN) 8.70 (1 H, d, J = 6.3 Hz, C_5H_3N), 8.68 (1 H, s, C_5H_3N), 8.54 (1 H, s, C_5H_3N), 8.45 (1 H, d, J = 6.8 Hz, C_5H_3N), 8.05 (1 H, d, J = 7.3 Hz, C_5H_3N), 7.96–7.89 (2 H, CH + C_5H_3N), 7.53 (2 H, d, J = 8.8 Hz, C_6H_4), 7.20–7.05 (2 H, m, 2CH), 6.77 (2 H, d, J = 8.8 Hz, C_6H_4), 6.75 (1 H, d, J = 15.1 Hz, CH), 4.98–4.93 (2 H, m, CH_2), 4.86–4.81 (2 H, m, CH_2), 3.04 (6 H, s, NMe_2), 2.80 (3 H, s, Me). Anal. Calcd (%) for $C_{25}H_{27}F_{12}N_3P_2$•0.3H_2O: C, 45.16; H, 4.18; N, 6.32. Found: C, 45.16; H, 4.25; N, 6.30. *m/z* = 514.4 ($[M - PF_6]^+$), 184.7 ($[M - 2PF_6]^{2+}$). A small amount of the corresponding disubstituted compound [**12**][PF_6]$_2$ (7 mg, 6%) was also obtained from the column.

Synthesis of 2-Methyl-11-[(*E*)-2-(2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)ethenyl]-6,7-dihydro-dipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium Hexafluorophosphate, [5][PF_6]$_2$. This compound was prepared and purified in manner similar to [**4**][PF_6]$_2$ by using Jdca (54 mg, 0.268 mmol) in place of (*E*)-4-(dimethylamino)cinnamaldehyde. The column was eluted with 48:6:1 to 35:4:1 acetone/water/saturated aqueous KNO_3 and a dark purple solid obtained: 52 mg, 28%; δ_H (300 MHz, CD_3CN) 8.69 (1 H, d, J = 6.4 Hz, C_5H_3N), 8.66 (1 H, s, C_5H_3N), 8.46 (1 H, s, C_5H_3N), 8.29 (1 H, d, J = 6.8 Hz, C_5H_3N), 8.05 (1 H, d, J = 6.2 Hz, C_3H_5N), 7.93 (1 H, d, J = 15.6 Hz, CH), 7.77 (1 H, d, J = 6.8 Hz, C_5H_3N), 7.25 (2 H, s, C_6H_2), 7.03 (1 H, d, J = 15.6 Hz, CH), 4.98–4.92 (2 H, m, CH_2), 4.80–4.74 (2 H, m, CH_2), 3.39 (4 H, t, J = 5.5 Hz, $2CH_2^{Jd}$), 2.83–2.75 (7 H, Me + $2CH_2^{Jd}$), 2.01–1.91 (4 H, m, $2CH_2^{Jd}$ overlapped with solvent signal). Anal. Calcd (%) for $C_{27}H_{29}F_{12}N_3P_2$: C, 47.31; H, 4.26; N, 6.13. Found: C, 47.50; H, 4.24; N, 6.23. *m/z* = 540.3 ($[M - PF_6]^+$), 197.9 ($[M - 2PF_6]^{2+}$). A small amount of the corresponding disubstituted compound [**13**][PF_6]$_2$ (4 mg, 3%) was also obtained from the column.

Synthesis of 2-Methyl-11-[(*E*)-4-(2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)buta-1,3-dienyl]-6,7-dihydro-dipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium Hexafluorophosphate, [6][PF_6]$_2$. This compound was prepared and purified in manner similar to [**4**][PF_6]$_2$ by using Jdpa (61 mg, 0.268 mmol) in place of (*E*)-4-(dimethylamino)cinnamaldehyde. The column was eluted with 35:4:1 acetone/water/saturated aqueous KNO_3 and a near black solid obtained: 62 mg, 32%; δ_H (500 MHz, CD_3CN) 8.68 (1 H, d, J = 5.7 Hz, C_5H_3N), 8.66 (1 H, s, C_5H_3N), 8.45 (1 H, s, C_5H_3N), 8.35 (1 H, d, J = 6.6 Hz, C_5H_3N), 8.03 (1 H, d, J = 6.0 Hz, C_3H_5N), 7.93–7.88 (1 H, m, CH), 7.80 (1 H, d, J = 6.9 Hz, C_5H_3N), 7.10 (2 H, s, C_6H_2), 7.10–6.97 (2 H, m, 2CH), 6.65 (1 H, d, J = 15.1 Hz, CH), 4.96–4.91 (2 H, m, CH_2), 4.80–4.76 (2 H, m, CH_2), 3.30 (4 H, t, J = 5.4 Hz, $2CH_2^{Jd}$), 2.79 (3 H, s, Me), 2.73 (4 H, t, J = 6.0 Hz, $2CH_2^{Jd}$), 1.97–1.89 (4 H, m, $2CH_2^{Jd}$ overlapped with solvent signal). Anal. Calcd (%) for $C_{29}H_{32}F_{12}N_3P_2$•0.5H_2O: C, 48.34; H, 4.48; N, 5.83. Found: C, 48.07; H, 4.56; N, 5.87. *m/z* = 566.3 ($[M - PF_6]^+$), 210.9 ($[M - 2PF_6]^{2+}$).

Synthesis of 2-Methyl-12-[(*E*)-2-(4-dimethylaminophenyl)ethenyl]-7,8-dihydro-6*H*-dipyrido[1,2-*a*:2′,1′-*c*]-[1,4]diazepinium Hexafluorophosphate, [7][PF_6]$_2$. This compound was prepared and purified in manner similar to [**4**][PF_6]$_2$ by using [PDQ^{2+}]Br_2 (104 mg, 0.269 mmol) in place of [EDQ^{2+}]Br_2 and 4-(dimethylamino)benzaldehyde (40 mg,

0.268 mmol) in place of (*E*)-4-(dimethylamino)cinnamaldehyde. The column was eluted with 35:4:1 to 16:2:1 acetone/water/saturated aqueous KNO_3 and reprecipitation gave a dark purple solid: 12 mg, 7%; δ_H (500 MHz, CD_3CN) 8.74 (1 H, d, J = 6.3 Hz , C_5H_3N), 8.46 (1 H, d, J = 6.3 Hz, C_5H_3N), 8.20 (1 H, s, C_5H_3N), 8.12 (1 H, s, C_5H_3N), 8.09 (1 H, d, J = 6.6 Hz, C_5H_3N), 7.96–7.90 (2 H, CH + C_5H_3N), 7.64 (2 H, d, J = 8.8 Hz, C_6H_4), 7.14 (1 H, d, J = 15.8 Hz, CH), 6.81 (2 H, d, J = 8.8 Hz, C_6H_4), 4.80–4.74 (1 H, m, NCH_2^{eq}), 4.64–4.58 (1 H, m, NCH_2^{eq}), 4.40–4.32 (1 H, m, NCH_2^{ax}), 4.16–4.08 (1 H, m, NCH_2^{ax}), 3.08 (6 H, s, NMe_2), 2.77 (3 H, s, Me), 2.75–2.67 (2 H, m, CH_2). Anal. Calcd (%) for $C_{24}H_{27}F_{12}N_3P_2$•0.5H_2O: C, 43.91; H, 4.30; N, 6.40. Found: C, 43.86; H, 4.17; N, 6.42. *m/z* = 502.2 ($[M - PF_6]^+$), 178.4 ($[M - 2PF_6]^{2+}$). Note: A higher yield of [**7**][PF_6]$_2$ (ca. 20%) was isolated from a preparation of the corresponding disubstituted compound [**15**][PF_6]$_2$ (see below).

Synthesis of 2-Methyl-12-[(*E*)-4-(4-dimethylaminophenyl)buta-1,3-dienyl]-7,8-dihydro-6*H*-dipyrido[1,2-*a*:2′,1′-*c*]-[1,4]diazepinium Hexafluorophosphate, [8][PF_6]$_2$. To a solution of **1** (100 mg, 0.293 mmol) in chloroform (20 mL) was added 1,3-bis(triflyloxy)propane (200 mg, 0.588 mmol) in dry dichloromethane (2 mL). The reaction was stirred at room temperature for 48 h, during which time the solution color changed to deep purple and a dark precipitate formed. The volume was reduced to ca. 5 mL under vacuum and diethyl ether added to ensure complete precipitation of the crude triflate salt which was filtered off and washed with diethyl ether. This solid was dissolved in methanol and aqueous NH_4PF_6 added to precipitate the product which was filtered off and washed with water. Purification of the crude product (150 mg) was effected as for [**4**][PF_6]$_2$ by column chromatography, but eluting with 48:6:1 acetone/water/saturated aqueous KNO_3, followed by reprecipitation to afford a dark purple solid: 65 mg, 32%; δ_H (400 MHz, CD_3CN) 8.74 (1 H, d, J = 6.3 Hz, C_5H_3N), 8.48 (1 H, d, J = 6.6 Hz, C_5H_3N), 8.19 (1 H, s, C_5H_3N), 8.11–8.07 (2 H, m, C_5H_3N), 7.94 (1 H, d, J = 6.6 Hz, C_5H_3N), 7.86–7.78 (1 H, m, CH), 7.51 (2 H, d, J = 8.8 Hz, C_6H_4), 7.17–7.02 (2 H, m, 2CH), 6.76 (2 H, d, J = 9.0 Hz, C_6H_4), 6.74 (1 H, d, J = 15.4 Hz, CH), 4.80–4.74 (1 H, m, NCH_2^{eq}), 4.65–4.58 (1 H, m, NCH_2^{eq}), 4.38–4.30 (1 H, m, NCH_2^{ax}), 4.17–4.08 (1 H, m, NCH_2^{ax}), 3.03 (6 H, s, NMe_2), 2.77 (3 H, s, Me), 2.75–2.67 (2 H, m, CH_2). Anal. Calcd (%) for $C_{26}H_{29}F_{12}N_3P_2$•0.8H_2O: C, 45.40; H, 4.48; N, 6.11. Found: C, 45.38; H, 4.09; N, 6.11. *m/z* = 528.4 ($[M - PF_6]^+$), 191.7 ($[M - 2PF_6]^{2+}$).

Synthesis of 2-Methyl-12-[(*E*)-2-(2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)ethenyl]-7,8-dihydro-6*H*-dipyrido[1,2-*a*:2′,1′-*c*]-[1,4]diazepinium Hexafluorophosphate, [9][PF_6]$_2$. This compound was prepared and purified in manner similar to [**7**][PF_6]$_2$ by using Jdca (54 mg, 0.269 mmol) in place of 4-(dimethylamino)benzaldehyde. The column was eluted with 35:4:1 acetone/water/saturated aqueous KNO_3 and a dark blue solid obtained: 32 mg, 17%; δ_H (300 MHz, CD_3CN) 8.73 (1 H, d, J = 6.4 Hz, C_5H_3N), 8.31 (1 H, d, J = 6.9 Hz, C_5H_3N), 8.18 (1 H, s, C_5H_3N), 8.07 (1 H, d, J = 6.8 Hz, C_3H_5N), 7.98 (1 H, s, C_5H_3N), 7.83–7.77 (2 H, C_5H_3N + CH), 7.20 (2 H, s, C_6H_2), 6.99 (1 H, d, J = 15.8 Hz, CH), 4.80–4.72 (1 H, m, NCH_2^{eq}), 4.58–4.49 (1 H, m, NCH_2^{eq}), 4.42–4.30 (1 H, m, NCH_2^{ax}), 4.11–3.98 (1 H, m, NCH_2^{ax}), 3.34 (4 H, t, J = 6.0 Hz, $2CH_2^{Jd}$), 2.79–2.60 (9 H, Me + CH_2 + $2CH_2^{Jd}$), 1.97–1.89 (4 H, m, $2CH_2^{Jd}$ overlapped with solvent signal). Anal. Calcd (%) for

$C_{28}H_{31}F_{12}N_3P_2$•0.5H_2O: C, 47.47; H, 4.55; N, 5.93. Found: C, 47.64; H, 4.32; N, 6.34. *m/z* = 544.4 ($[M - PF_6]^+$), 204.8 ($[M - 2PF_6]^{2+}$).

Synthesis of 2-Methyl-12-[(*E*)-4-(2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)buta-1,3-dienyl]-7,8-dihydro-6*H*-dipyrido[1,2-*a*:2′,1′-*c*]-[1,4]diazepinium Hexafluorophosphate, [10][PF_6]$_2$. This compound was prepared and purified in manner similar to [**7**][PF_6]$_2$ by using Jdpa (61 mg, 0.268 mmol) in place of 4-(dimethylamino)benzaldehyde. The column was eluted with 48:6:1 to 16:2:1 acetone/water/saturated aqueous KNO_3 and a dark red-brown solid obtained: 49 mg, 24%; δ_H (500 MHz, CD_3CN) 8.75 (1 H, d, *J* = 6.3 Hz, C_5H_3N), 8.40 (1 H, d, *J* = 6.9 Hz, C_5H_3N), 8.19 (1 H, s, C_5H_3N), 8.08 (1 H, d, *J* = 6.3 Hz, C_3H_5N), 8.02 (1 H, s, C_5H_3N), 7.86–7.78 (2 H, C_5H_3N + CH), 7.07 (2 H, s, C_6H_2), 7.06–6.94 (2 H, m, 2CH), 6.65 (1 H, d, *J* = 14.8 Hz, CH), 4.80–4.74 (1 H, m, NCH_2^{eq}), 4.60–4.54 (1 H, m, NCH_2^{eq}), 4.39–4.32 (1 H, m, NCH_2^{ax}), 4.13–4.05 (1 H, m, NCH_2^{ax}), 3.28 (4 H, t, *J* = 5.7 Hz, $2CH_2^{Jd}$), 2.77 (3 H, s, Me), 2.74–2.65 (6 H, CH_2 + $2CH_2^{Jd}$), 1.94–1.88 (4 H, m, $2CH_2^{Jd}$ overlapped with solvent signal). Anal. Calcd (%) for $C_{30}H_{33}F_{12}N_3P_2$•1.4H_2O: C, 48.00; H, 4.81; N, 5.60. Found: C, 48.02; H, 4.43; N, 5.60. *m/z* = 580.3 ($[M - PF_6]^+$), 217.9 ($[M - 2PF_6]^{2+}$).

Synthesis of 2,11-Bis[(*E*)-2-(4-dimethylaminophenyl)ethenyl]-6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium Hexafluorophosphate, [11][PF_6]$_2$. This compound was prepared in manner similar to [**3**][PF_6]$_2$ by using 4-(dimethylamino)benzaldehyde (801 mg, 5.37 mmol) and a reaction time of 28 h. After cooling to room temperature, a brown precipitate was filtered off and the blue filtrate containing [**3**][PF_6]$_2$ was discarded. This crude dibromide product was converted to its PF_6^- salt and purified as for [**3**][PF_6]$_2$ to afford a dark purple solid: 110 mg, 51%; δ_H (400 MHz, CD_3CN) 8.63 (2 H, s, C_5H_3N), 8.40 (2 H, d, *J* = 6.8 Hz, C_5H_3N), 8.06 (2 H, d, *J* = 15.6 Hz, 2CH), 7.89 (2 H, d, *J* = 6.1 Hz, C_5H_3N), 7.67 (4 H, d, *J* = 8.8 Hz, $2C_6H_4$), 7.16 (2 H, d, *J* = 15.6 Hz, 2CH), 6.84 (4 H, d, *J* = 8.8 Hz, $2C_6H_4$), 4.79 (4 H, s, $2CH_2$), 3.10 (12 H, s, $2NMe_2$). Anal. Calcd (%) for $C_{32}H_{34}F_{12}N_4P_2$•1.7H_2O: C, 48.33; H, 4.74; N, 7.05. Found: C, 48.33; H, 4.57; N, 6.92. *m/z* = 619.5 ($[M - PF_6]^+$), 237.3 ($[M - 2PF_6]^{2+}$).

Synthesis of 2,11-Bis[(*E*)-4-(4-dimethylaminophenyl)buta-1,3-dienyl]-6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium Hexafluorophosphate, [12][PF_6]$_2$. This compound was prepared and purified in manner similar to [**4**][PF_6]$_2$ by using (*E*)-4-(dimethylamino)cinnamaldehyde (471 mg, 2.69 mmol) in methanol (20 mL) and a reaction time of 40 h. The column was eluted with 20:4:1 acetone/water/saturated aqueous KNO_3 and a dark purple solid obtained: 33 mg, 15%; δ_H (400 MHz, CD_3CN) 8.57 (2 H, s, C_5H_3N), 8.43 (2 H, d, *J* = 6.6 Hz, C_5H_3N), 7.98–7.88 (4 H, C_5H_3N + 2CH), 7.54 (4 H, d, *J* = 8.8 Hz, $2C_6H_4$), 7.21–7.06 (4 H, 4CH), 6.78 (4 H, d, *J* = 9.1 Hz, $2C_6H_4$), 6.76 (2 H, d, *J* = 15.4 Hz, 2CH), 4.80 (4 H, s, $2CH_2$), 3.04 (12 H, s, $2NMe_2$). Anal. Calcd (%) for $C_{36}H_{38}F_{12}N_4P_2$•1.2H_2O: C, 51.58; H, 4.86; N, 6.68. Found: C, 51.48; H, 4.68; N, 6.99. *m/z* = 671.5 ($[M - PF_6]^+$), 263.3 ($[M - 2PF_6]^{2+}$). Note: of the major purple band (141 mg) eluted from the column, only the last fractions were of adequate purity. The actual yield of this reaction is thus several times that quoted above.

Synthesis of 2,11-Bis[(*E*)-2-(2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)ethenyl]-6,7-dihydro-dipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium Hexafluorophosphate, [13][PF$_6$]$_2$. This compound was prepared and purified in manner similar to [**12**][PF$_6$]$_2$ by using Jdca (432 mg, 2.15 mmol) in place of (*E*)-4-(dimethylamino)cinnamaldehyde. The column was eluted with 35:4:1 acetone/water/saturated aqueous KNO_3 and a dark blue solid obtained: 74 mg, 32%; δ_H (300 MHz, CD_3CN) 8.46 (2 H, s, C_5H_3N), 8.24 (2 H, d, J = 6.8 Hz, C_5H_3N), 7.91 (2 H, d, J = 15.3 Hz, 2CH), 7.73 (2 H, d, J = 7.0 Hz, C_5H_3N), 7.23 (4 H, s, $2C_6H_2$), 7.01 (2 H, d, J = 15.3 Hz, 2CH), 4.70 (4 H, s, $2CH_2$), 3.35 (8 H, t, J = 5.7 Hz, $4CH_2^{Jd}$), 2.76 (8 H, t, J = 6.2 Hz, $4CH_2^{Jd}$), 1.99–1.89 (8 H, m, $4CH_2^{Jd}$ overlapped with solvent signal). Anal. Calcd (%) for $C_{40}H_{42}F_{12}N_4P_2$: C, 55.30; H, 4.87; N, 6.45. Found: C, 55.32; H, 4.97; N, 6.56. *m/z* = 723.1 ([M – PF$_6$]$^+$), 289.4 ([M – 2PF$_6$]$^{2+}$).

Synthesis of 2,11-Bis[(*E*)-2-(2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)ethenyl]-6,7-dihydro-dipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium Trifluoromethane-sulfonate, [13][OTf]$_2$. To a solution of [**13**][PF$_6$]$_2$ (20 mg, 0.023 mmol) in acetone (5 mL) was added saturated [N(C_4H_9-*n*)$_4$]Cl in acetone. The precipitate of [**13**]Cl$_2$ was filtered off, washed with acetone, then dissolved in a minimum of methanol. Saturated aqueous NaOTf was added, precipitating crude [**13**][OTf]$_2$ (19.6 mg, 94%) which was filtered off and air dried. Purification was effected by vapor diffusion of diethyl ether into an acetonitrile solution at room temperature, giving dark blue [**13**][OTf]$_2$•MeCN as a mixture of microcrystalline material and X-ray diffraction quality crystals: 9 mg, 43%; δ_H (400 MHz, CD_3CN) 8.66 (2 H, s, C_5H_3N), 8.23 (2 H, d, J = 6.8 Hz, C_5H_3N), 8.01 (2 H, d, J = 15.6 Hz, 2CH), 7.70 (2 H, d, J = 6.8 Hz, C_5H_3N), 7.23 (4 H, s, $2C_6H_2$), 7.01 (2 H, d, J = 15.6 Hz, 2CH), 4.68 (4 H, s, $2CH_2$), 3.34 (8 H, t, J = 5.7 Hz, $4CH_2^{Jd}$), 2.72 (8 H, t, J = 6.1 Hz, $4CH_2^{Jd}$), 1.97–1.87 (8 H, m, $4CH_2^{Jd}$ overlapped with solvent signal). Anal. Calcd (%) for $C_{42}H_{42}F_6N_4O_6S_2$•1.5H_2O: C, 55.80; H, 5.02; N, 6.20. Found: C, 55.91; H, 4.69; N, 5.82. NB: drying under vacuum results in loss of acetonitrile which is then replaced by atmospheric water. *m/z* = 727.9 ([M – OTf]$^+$), 289.3 ([M – 2OTf]$^{2+}$).

Synthesis of 2,11-Bis[(*E*)-4-(2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)buta-1,3-dienyl]-6,7-dihydro-dipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium Hexafluoro-phosphate, [14][PF$_6$]$_2$. This compound was prepared and purified in manner similar to [**12**][PF$_6$]$_2$ by using Jdpa (488 mg, 2.15 mmol) in place of (*E*)-4-(dimethylamino)cinnamaldehyde. The column was eluted with 48:6:1 to 35:4:1 acetone/water/saturated aqueous KNO_3 and a dark blue solid obtained: 89 mg, 35%; δ_H (500 MHz, CD_3CN) 8.47 (2 H, s, C_5H_3N), 8.31 (2 H, d, J = 6.6 Hz, C_5H_3N), 7.94–7.84 (2 H, m, 2CH), 7.79 (2 H, d, J = 6.9 Hz, C_5H_3N), 7.11 (4 H, s, $2C_6H_2$), 7.09–6.96 (4 H, m, 4CH), 6.66 (2 H, d, J = 15.1 Hz, 2CH), 4.74 (4 H, s, $2CH_2$), 3.30 (8 H, t, J = 5.5 Hz, $4CH_2^{Jd}$), 2.74 (8 H, t, J = 6.0 Hz, $4CH_2^{Jd}$), 1.96–1.89 (8 H, m, $4CH_2^{Jd}$ overlapped with solvent signal). Anal. Calcd (%) for $C_{44}H_{46}F_{12}N_4P_2$•0.8H_2O: C, 56.51; H, 5.13; N, 5.99. Found: C, 56.36; H, 5.12; N, 6.36. *m/z* = 775.5 ([M – PF$_6$]$^+$), 315.4 ([M – 2PF$_6$]$^{2+}$).

Synthesis of 2,12-Bis[(*E*)-2-(4-dimethylaminophenyl)ethenyl]-7,8-dihydro-6*H*-dipyrido[1,2-*a*:2′,1′-*c*]-[1,4]diazepinium Hexafluorophosphate, [15][PF$_6$]$_2$. This

compound was prepared in manner similar to [**3**][PF_6]$_2$ by using [PDQ^{2+}]Br_2 (204 mg, 0.528 mmol) in place of [EDQ^{2+}]Br_2 and 4-(dimethylamino)benzaldehyde (1.60 g, 10.72 mmol) in methanol (50 mL) with pyridine (6 drops) and a reaction time of 40 h. After reducing the volume to 20 mL and cooling to room temperature, a brown precipitate was filtered off. This crude dibromide product was converted to its PF_6^- salt and purified as for [**3**][PF_6]$_2$ to afford a dark purple solid: 213 mg, 50%; δ_H (500 MHz, CD_3CN) 8.45 (2 H, d, J = 6.6 Hz, C_5H_3N), 8.21 (2 H, s, C_5H_3N), 7.99–7.91 (4 H, C_5H_3N + 2CH), 7.64 (4 H, d, J = 8.8 Hz, $2C_6H_4$), 7.16 (2 H, d, J = 16.1 Hz, 2CH), 6.81 (4 H, d, J = 8.8 Hz, $2C_6H_4$), 4.65–4.57 (2 H, m, NCH_2^{eq}), 4.27–4.17 (2 H, m, NCH_2^{ax}), 3.08 (12 H, s, $2NMe_2$), 2.70–2.62 (2 H, m, CH_2). Anal. Calcd (%) for $C_{33}H_{36}F_{12}N_4P_2$•1.5H_2O: C, 49.20; H, 4.88; N, 6.95. Found: C, 49.16; H, 4.64; N, 6.78. *m/z* = 633.3 ([M – PF_6]$^+$), 244.4 ([M – 2PF_6]$^{2+}$). Note: the methanol filtrate obtained after removal of the brown precipitate was also treated with aqueous NH_4PF_6, giving further solid material which was subjected to silica gel column chromatography, eluting with 48:6:1 to 35:4:1 acetone/water/saturated aqueous KNO_3; this yielded further [**15**][PF_6]$_2$ (46 mg) and also [**7**][PF_6]$_2$ (68 mg, 20% if •0.5H_2O).

Synthesis of 2,12-Bis[(*E*)-2-(4-dimethylaminophenyl)ethenyl]-7,8-dihydro-6*H*-dipyrido[1,2-*a*:2′,1′-*c*]-[1,4]diazepinium 2-Naphthalenesulfonate, [15][$NapSO_3$]$_2$. To a solution of [**15**][PF_6]$_2$•1.5H_2O (80 mg, 0.099 mmol) in acetonitrile (15 mL) was added saturated [$N(C_4H_9$-*n*$)_4$]$NapSO_3$ in acetone (3 mL). Acetone was added (20 mL) and the solution was cooled in a refrigerator for 2 h. The red-brown precipitate was filtered off, washed with acetone and air dried (87 mg). This material was redissolved in acetonitrile (100 mL), the solution filtered to remove a dark brown-black impurity, and the product reprecipitated by addition of diethyl ether to give a dark red microcrystalline powder: 76 mg, 81%; δ_H (400 MHz, $(CD_3)_2SO$) 8.92 (2 H, d, J = 6.6 Hz, C_5H_3N), 8.50 (2 H, s, C_5H_3N), 8.20 (2 H, d, J = 6.1 Hz, C_5H_3N), 8.15–8.08 (4 H, 2CH + Nap), 7.98–7.93 (2 H, m, Nap), 7.92–7.87 (2 H, m, Nap), 7.85 (2 H, d, J = 8.6 Hz, Nap), 7.70 (2 H, d, J = 8.6 Hz, Nap), 7.64 (4 H, d, J = 9.1 Hz, $2C_6H_4$), 7.54–7.49 (4 H, m, Nap), 7.30 (2 H, d, J = 15.9 Hz, 2CH), 6.82 (4 H, d, J = 8.8 Hz, $2C_6H_4$), 4.82–4.73 (2 H, m, NCH_2^{eq}), 4.39–4.28 (2 H, m, NCH_2^{ax}), 3.05 (12 H, s, $2NMe_2$), 2.67–2.55 (2 H, m, CH_2). Anal. Calcd (%) for $C_{53}H_{50}N_4O_6S_2$•2.8H_2O: C, 66.76; H, 5.88; N, 5.88. Found: C, 66.60; H, 5.61; N, 5.95. *m/z* = 695.6 ([M – $NapSO_3$]$^+$), 244.4 ([M – 2$NapSO_3$]$^{2+}$). Note: this material is hygroscopic; analysis on both single crystals of [**15**][$NapSO_3$]$_2$•2H_2O (hydration level determined by X-ray crystallography, see below) and microcrystalline material gives similar values. Thermogravimetric analysis indicates 4.7% water, consistent with ca. 2.5 H_2O molecules per formula unit.

Synthesis of 2,12-Bis[(*E*)-4-(4-dimethylaminophenyl)buta-1,3-dienyl]-7,8-dihydro-6*H*-dipyrido[1,2-*a*:2′,1′-*c*]-[1,4]diazepinium Hexafluorophosphate, [16][PF_6]$_2$. This compound was prepared and purified in manner similar to [**8**][PF_6]$_2$ by using **2** (241 mg, 0.483 mmol) in place of **1** and 1,3-bis(triflyloxy)propane (329 mg, 0.967 mmol). Due to the poor solubility of **2**, 50 mL of chloroform was used and the reaction carried out at reflux. The column was eluted with 35:4:1 acetone/water/saturated aqueous KNO_3, and reprecipitation afforded a dark purple solid: 158 mg, 39%; δ_H (400 MHz, CD_3CN) 8.47 (2 H,

d, J = 6.8 Hz, C_5H_3N), 8.17 (2 H, s, C_5H_3N), 7.92 (2 H, d, J = 6.6 Hz, C_5H_3N), 7.89–7.82 (2 H, m, 2CH), 7.51 (4 H, d, J = 8.8 Hz, $2C_6H_4$), 7.17–7.03 (4 H, m, 4CH), 6.79–6.73 (6 H, $2C_6H_4$ + 2CH), 4.66–4.58 (2 H, m, NCH_2^{eq}), 4.27–4.16 (2 H, m, NCH_2^{ax}), 3.03 (12 H, s, $2NMe_2$), 2.71–2.62 (2 H, m, CH_2). Anal. Calcd (%) for $C_{37}H_{40}F_{12}N_4P_2$•$0.8H_2O$: C, 52.59; H, 4.96; N, 6.63. Found: C, 52.58; H, 4.65; N, 6.54. *m/z* = 685.4 ($[M - PF_6]^+$), 270.4 ($[M - 2PF_6]^{2+}$).

Synthesis of 2,12-Bis[(*E*)-4-(4-dimethylaminophenyl)buta-1,3-dienyl]-7,8-dihydro-6*H*-dipyrido[1,2-*a*:2′,1′-*c*]-[1,4]diazepinium 2-Naphthalenesulfonate, [16][$NapSO_3$]$_2$. This compound was prepared in manner similar to [**15**][$NapSO_3$]$_2$ by using [**16**][PF_6]$_2$•$0.8H_2O$ (21 mg, 0.025 mmol) in place of [**15**][PF_6]$_2$•$1.5H_2O$ in acetonitrile (3 mL). Crystallization of the crude material (15 mg, 60%) by vapor diffusion of diethyl ether into a 1:4 methanol/acetone solution at room temperature produced brown rod-like crystals: 10 mg, 40%; δ_H (400 MHz, $(CD_3)_2SO$) 8.94 (2 H, d, J = 6.6 Hz, C_5H_3N), 8.45 (2 H, s, C_5H_3N), 8.22 (2 H, d, J = 6.6 Hz, C_5H_3N), 8.13 (2 H, s, Nap), 8.03–7.93 (4 H, 2CH + Nap), 7.92–7.87 (2 H, m, Nap), 7.85 (2 H, d, J = 8.6 Hz, Nap), 7.70 (2 H, d, J = 8.6 Hz, Nap), 7.54–7.48 (8 H, $2C_6H_4$ + Nap), 7.15–7.06 (4 H, m, 4CH), 6.83 (2 H, d, J = 15.0 Hz, 2CH), 6.74 (2 H, d, J = 9.1 Hz, $2C_6H_4$), 4.83–4.74 (2 H, m, NCH_2^{eq}), 4.40–4.28 (2 H, m, NCH_2^{ax}), 3.35 (12 H, s, $2NMe_2$), 2.68–2.56 (2 H, m, CH_2). Anal. Calcd (%) for $C_{57}H_{54}N_4O_6S_2$•$4H_2O$: C, 66.64; H, 6.08; N, 5.45. Found: C, 66.63; H, 5.70; N, 5.47. *m/z* = 748.1 ($[M - NapSO_3]^+$), 270.4 ($[M - 2NapSO_3]^{2+}$). Note: this salt is hygroscopic, in similar manner to [**15**][$NapSO_3$]$_2$.

Synthesis of 2,12-Bis[(*E*)-2-(2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)ethenyl]-7,8-dihydro-6*H*-dipyrido[1,2-*a*:2′,1′-*c*]-[1,4]diazepinium Hexafluorophosphate, [17][PF_6]$_2$. This compound was prepared and purified in manner similar to [**12**][PF_6]$_2$ by using [PDQ^{2+}]Br_2 (104 mg, 0.269 mmol) in place of [EDQ^{2+}]Br_2 and Jdca (432 mg, 2.15 mmol) in place of (*E*)-4-(dimethylamino)cinnamaldehyde. The column was eluted with 35:4:1 acetone/water/saturated aqueous KNO_3 and a dark blue solid obtained: 43 mg, 18%; δ_H (500 MHz, CD_3CN) 8.30 (2 H, d, J = 6.9 Hz, C_5H_3N), 8.06 (2 H, s, C_5H_3N), 7.82 (2 H, d, J = 14.8 Hz, CH), 7.77 (2 H, d, J = 7.2 Hz, C_5H_3N), 7.20 (4 H, s, $2C_6H_2$), 7.00 (2 H, d, J = 15.4 Hz, 2CH), 4.55–4.48 (2 H, m, NCH_2^{eq}), 4.20–4.12 (2 H, m, NCH_2^{ax}), 3.34 (8 H, t, J = 5.6 Hz, $4CH_2^{Jd}$), 2.74 (8 H, t, J = 6.6 Hz, $4CH_2^{Jd}$), 2.63–2.54 (2 H, m, CH_2) 1.98–1.90 (8 H, m, $4CH_2^{Jd}$ overlapped with solvent signal). Anal. Calcd (%) for $C_{41}H_{44}F_{12}N_4P_2$•$0.9H_2O$: C, 54.78; H, 5.14; N, 6.23. Found: C, 54.78; H, 4.89; N, 6.30. *m/z* = 737.4 ($[M - PF_6]^+$), 296.6 ($[M - 2PF_6]^{2+}$).

Synthesis of 2,12-Bis[(*E*)-4-(2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)buta-1,3-dienyl]-7,8-dihydro-6*H*-dipyrido[1,2-*a*:2′,1′-*c*]-[1,4]diazepinium Hexafluorophosphate, [18][PF_6]$_2$. This compound was prepared and purified in manner similar to [**17**][PF_6]$_2$ by using Jdpa (488 mg, 2.15 mmol) in place of Jdca. The column was eluted with 48:6:1 acetone/water/saturated aqueous KNO_3 and a dark blue solid obtained: 68 mg, 27%; δ_H (500 MHz, CD_3CN) 8.36 (2 H, d, J = 6.3 Hz, C_5H_3N), 8.08 (2 H, s, C_5H_3N), 7.94–7.85 (4 H, C_5H_3N + 2CH), 7.08 (4 H, s, $2C_6H_2$), 7.06–6.95 (4 H, m, 4CH), 6.65 (2 H, d, J = 15.5 Hz, 2CH), 4.60–4.53 (2 H, m, NCH_2^{eq}), 4.20–4.14 (2 H, m, NCH_2^{ax}), 3.28 (8 H, t, J = 6.0 Hz,

$4CH_2^{Jd}$), 2.72 (8 H, t, J = 6.0 Hz, $4CH_2^{Jd}$), 2.64–2.58 (2 H, m, CH_2) 1.97–1.89 (8 H, m, $4CH_2^{Jd}$ overlapped with solvent signal). Anal. Calcd (%) for $C_{45}H_{48}F_{12}N_4P_2$•$0.7H_2O$: C, 57.05; H, 5.26; N, 5.91. Found: C, 56.98; H, 4.99; N, 5.82. *m/z* = 789.5 ($[M - PF_6]^+$), 322.8 ($[M - 2PF_6]^{2+}$).

X-Ray Crystallography. Crystals were obtained by diffusion of diethyl ether vapor into solutions at room temperature, using acetonitrile ([**13**][OTf]$_2$•2MeCN and [**17**][PF_6]$_2$•2MeCN), acetone ([**8**][PF_6]$_2$•Me_2CO and [**18**][PF_6]$_2$•$2Me_2CO$) or 4:1 acetone/methanol ([**16**][$NapSO_3$]$_2$•$2H_2O$). In some cases, the diffusion rate was slowed by using a lid spiked with small holes. Crystals of [**15**][$NapSO_3$]$_2$•$2H_2O$ formed by slow evaporation of the approximately 1:1 acetone/acetonitrile filtrate obtained after removal of most of the crude material (see above). Data for most of the crystals were collected on Oxford Diffraction XCalibur 2 or Bruker APEX II CCD X-ray diffractometers using MoK_α radiation (λ = 0.71073 Å), but the crystals of [**16**][$NapSO_3$]$_2$•$2H_2O$ and [**18**][PF_6]$_2$•$2Me_2CO$ were small and very weakly diffracting, so were analyzed by using Station 9.8 at the Synchrotron Radiation Source, Daresbury Laboratory, Warrington, Cheshire, U.K. (λ = 0.6945 Å). The data were processed by using the Oxford Diffraction CrysAlis RED[6] or Bruker SAINT[7] and SADABS[8] software packages. Many crystalline samples obtained were weakly diffracting; the six that afforded 99% complete data to 1.0 Å resolution or better are presented in the article; weaker datasets used primarily for space group determinations (for the salts [**7**][$NapSO_3$]$_2$, [**7**][PF_6]$_2$•MeCN and [**9**][PF_6]$_2$•MeCN, from crystals obtained by diffusion of diethyl ether vapor into acetonitrile solutions at room temperature) are included in the CIF provided as Supporting Information.

The structures were solved by direct methods by using SIR-97[9a] or SIR-2004[9b] via WinGX,[10] or SHELXS-97,[11] and refined by full-matrix least-squares on all F_0^2 data by using SHELXL-97.[12] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in idealized positions by using the riding model, with thermal parameters of 1.2 times those of aromatic parent carbon atoms, and 1.5 times those of methyl parent carbons. The asymmetric units have the following compositions: for [**8**][PF_6]$_2$•Me_2CO, one dication, two crystallographically independent PF_6^- anions and an acetone molecule; for [**13**][OTf]$_2$•2MeCN, half a dication, half of each disordered $CF_3SO_3^-$ anion and one acetonitrile molecule; for [**15**][$NapSO_3$]$_2$•$2H_2O$, half a dication, one $NapSO_3^-$ anion and one water molecule, with the complete cation generated by the mirror plane bisecting C1 and the bipyridyl unit; for [**16**][$NapSO_3$]$_2$•$2H_2O$, half a dication, one disordered $NapSO_3^-$ anion and one water molecule; for [**17**][PF_6]$_2$•2MeCN, half a dication, two half PF_6^- anions and one of the two acetonitrile molecules; for [**18**][PF_6]$_2$•$2Me_2CO$**,** half a dication, one PF_6^- anion and one acetone molecule. The crystal of [**16**][$NapSO_3$]$_2$•$2H_2O$ diffracted especially weakly; despite using synchrotron radiation, and attempts to solve in multiple space groups, the best resolution and $R1$ value that could be obtained were 0.90 Å and 11.4%, respectively. All other calculations were carried out by using the SHELXTL package.[13]

Hyper-Rayleigh Scattering. General details of the hyper-Rayleigh scattering (HRS) experiment have been discussed elsewhere,[14] and the experimental procedure and data

analysis protocol for the fs measurements used in this study were as previously described.[15] Measurements were carried out in acetonitrile, with crystal violet as an external octupolar reference ($\beta_{xxx,800}$ = 338 × 10^{-30} esu in methanol),[15a] and local field correction factors at optical frequencies are applied to correct for the difference in solvent. All measurements were performed by using the 800 nm fundamental of a regenerative mode-locked Ti^{3+}:sapphire laser (Spectra Physics, model Tsunami®, 100 fs pulses, 1 W, 80 MHz). Dilute solutions (10^{-4}–10^{-6} M) were used to ensure linear dependences of $I_{2\omega}/I_{\omega}^{2}$ on solute concentration, precluding the need for Lambert-Beer correction factors. The absence of frequency demodulation of the observed hyperpolarizability, i.e. constant values of β versus amplitude modulation frequency, showed that no fluorescence contributions to the HRS signals were present at 400 nm. This situation may indicate: *(i)* a lack of fluorescence, *(ii)* spectral filtering out of fluorescence, or *(iii)* the fluorescence lifetime is too short for its demodulation to be observed within the bandwidth of the instrument. The reported β values are the averages taken from measurements at different amplitude modulation frequencies. HRS depolarization ratios ρ[16] were determined at 800 nm in acetonitrile according to a published methodology.[17] While the precision of individual depolarization measurements is high (fitting errors of ca. ±0.02), multiple measurements on the crystal violet reference and on some of the samples indicated significant variability in the ρ values obtained. Hence the errors for the whole dataset have been estimated based on the variability of ca ±15% observed in the values obtained for the reference.

Stark Spectroscopy. The Stark apparatus, experimental methods and data collection procedure were as previously reported,[18] except that a Xe arc lamp was used as the light source in the place of a W filament bulb. The Stark spectrum for each compound was measured at least twice. For the MS compounds [**3**–**10**][PF_6]$_2$, the minor, relatively high energy ICT bands observed at room temperature are not evident at 77 K. Satisfactory fits of the Stark data for these salts were obtained by using the observed absorption (ε/ν vs ν) spectra, but for [**11**–**18**][PF_6]$_2$ these spectra were modeled with a sum of two or three Gaussian curves that reproduce the data and separate the peaks. The first and second derivatives of the Gaussian curves were then used to fit the Stark spectra with Liptay's equation.[19] The dipole-moment change $\Delta\mu_{12} = \mu_e - \mu_g$ (where μ_e and μ_g are the respective excited- and ground-state dipole moments, associated with each of the optical transitions considered in the fit) was then calculated from the coefficient of the second derivative component. Butyronitrile was used as the glassing medium, for which the local field correction f_{int} is estimated as 1.33.[18] In analyzing the resulting data in cases involving spectral deconvolution (i.e. for [**11**–**18**][PF_6]$_2$), for f_{os} and μ_{12} it is appropriate to consider the total values for the two or three components, since the superposition of these gives the overall absorption profile. However, when comparing values of $\Delta\mu_{12}$, $\Delta\mu_{ab}$, r_{12}, r_{ab}, c_b^2 and H_{ab}, it is necessary to derive averages because the fitted Gaussian components represent hypothetical ICT transitions that are codirectional, but not additive with respect to these parameters.

Computational Procedures. All theoretical calculations were performed by using the Gaussian 03[20] program. The molecular geometries were optimized by using the hybrid

functional B3P86[21] and the 6-31G*[22] basis set. The same model chemistry (B3P86/6-31G*) was used for TD-DFT calculations and the excited-state dipole moments were calculated by using the one particle RhoCI density. Molecular hyperpolarizabilities at zero frequency were calculated by the finite field (FF) approach using the B3P86/6-31G* model. The default Gaussian 03 parameters were used in every case. Molecular orbital contours were plotted by using Molekel 4.3.[23]

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2. Additional ^{1}H NMR Figure

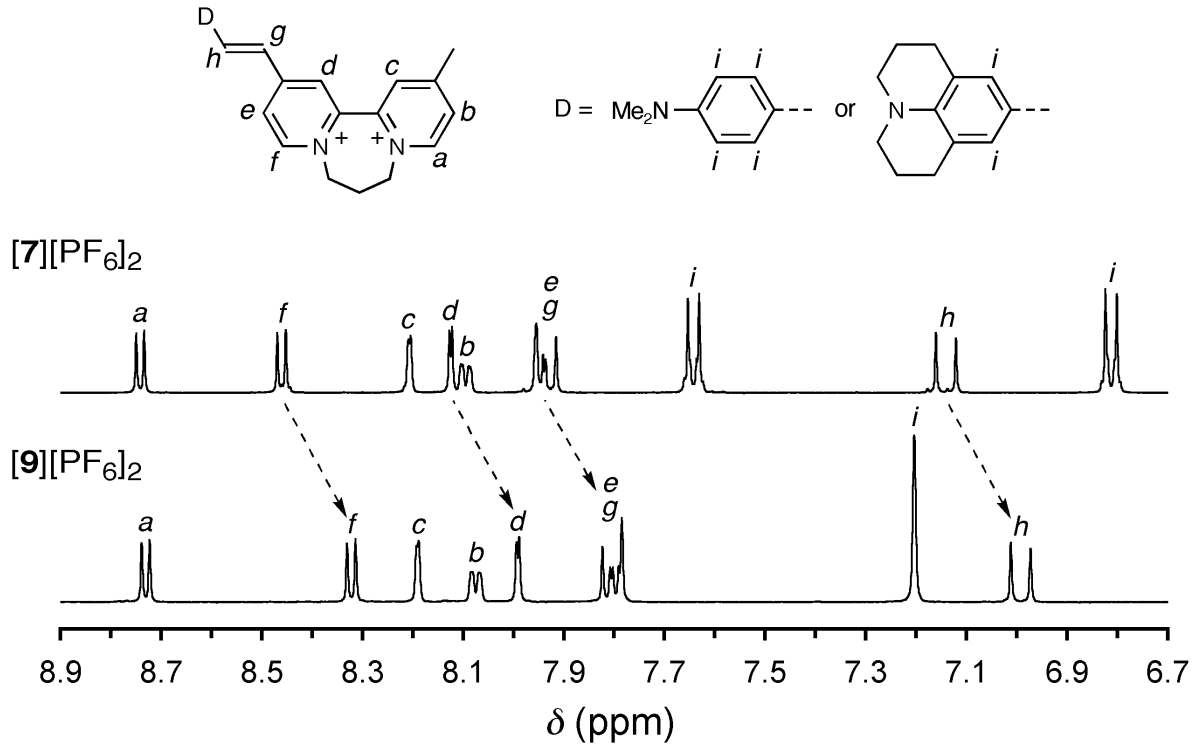

Figure S1. Aromatic regions of the ^{1}H NMR spectra of the salts [**7**][PF_6]$_2$ and [**9**][PF_6]$_2$ recorded at 400 MHz in CD_3CN at 293 K. The arrows indicate the largest shielding effects that are observed for the π-ED-side C_5H_3N and CH signals. The signal assignments are based on their relative positions and multiplicities.

3. Additional X-Ray Crystallographic Data and Figures

Table S1. Selected Interatomic Distances (Å) and Angles (deg) for the Salt [**8**][PF_6]$_2$•Me_2CO

N(1)–C(9)	1.485(3)	C(5)–C(10)	1.480(3)	C(18)–C(23)	1.442(3)
N(1)–C(14)	1.349(3)	C(10)–C(11)	1.371(3)	C(19)–C(20)	1.414(3)
N(1)–C(10)	1.366(3)	C(12)–C(13)	1.399(3)	C(23)–C(24)	1.346(3)
N(2)–C(1)	1.343(3)	C(13)–C(14)	1.361(3)	C(24)–C(25)	1.424(3)
N(2)–C(5)	1.367(3)	C(12)–C(26)	1.447(3)	C(25) –C(26)	1.345(3)
N(2)–C(7)	1.488(3)	C(15)–C(16)	1.404(3)		
C(1)–C(2)	1.372(3)	C(15) –C(20)	1.414(3)	C(12)–C(26)–C(25)	124.3(2)
C(2)–C(3)	1.381(3)	C(16)–C(17)	1.375(3)	C(26)–C(25)–C(24)	126.0(2)
C(3)–C(4)	1.403(3)	C(17)–C(18)	1.405(3)	C(25)–C(24)–C(23)	121.7(2)
C(4)–C(5)	1.374(3)	C(18)–C(19)	1.411 (3)	C(24)–C(23)–C(18)	128.5(2)

X-Ray Powder Diffraction for [15][$NapSO_3$]$_2$•$2H_2O$. Data were collected on a bulk sample of [**15**][$NapSO_3$]$_2$•$2H_2O$ at room temperature using a Philips X'PERT powder diffractometer with copper radiation (λ = 1.54056 Å). The data obtained are an excellent match for the pattern calculated for the single-crystal structure by using the Mercury software (Figure S1). The slight changes in peak positions can be accounted for by the difference in temperature between the two data collections; at room temperature, the unit cell is slightly expanded with the result that the diffraction peaks shift to lower angles when compared with those derived from the single-crystal data collection at 100 K.

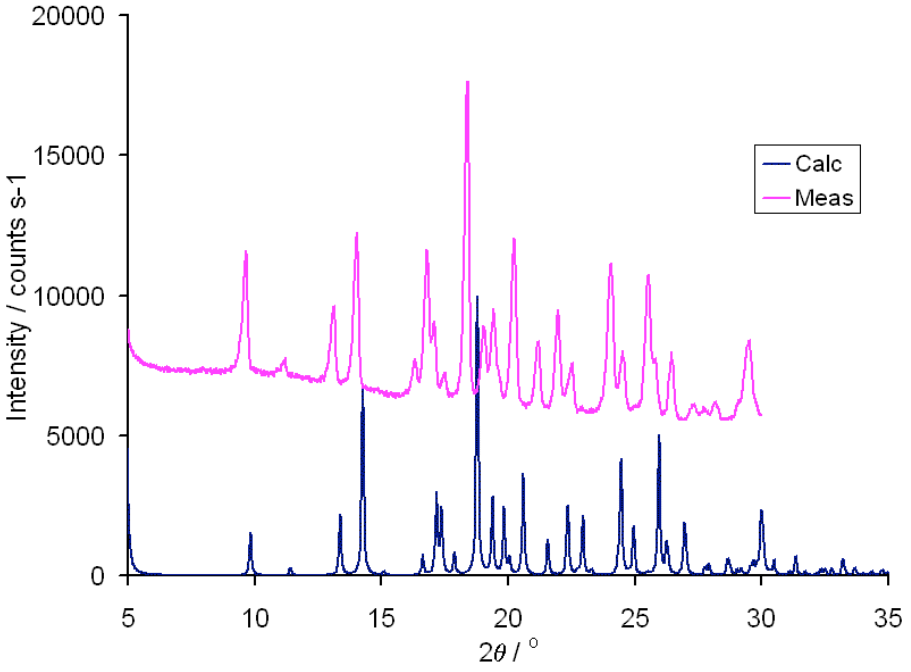

Figure S2. Calculated and measured X-ray powder diffraction data for [**15**][$NapSO_3$]$_2$•$2H_2O$.

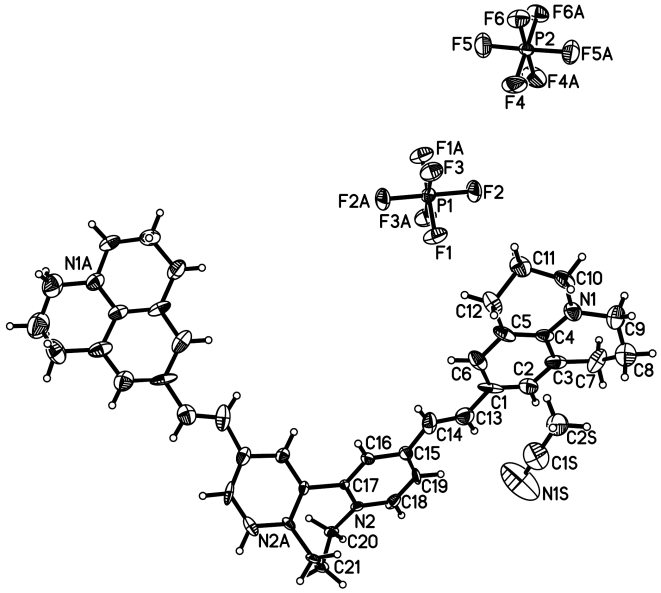

Figure S3. Representation of the molecular structure of [**17**][PF_6]$_2$•2MeCN (50% probability ellipsoids). While the dication and PF_6^- anions been completed by generating symmetry equivalent atoms, only the single acetonitrile molecule in the asymmetric unit is shown.

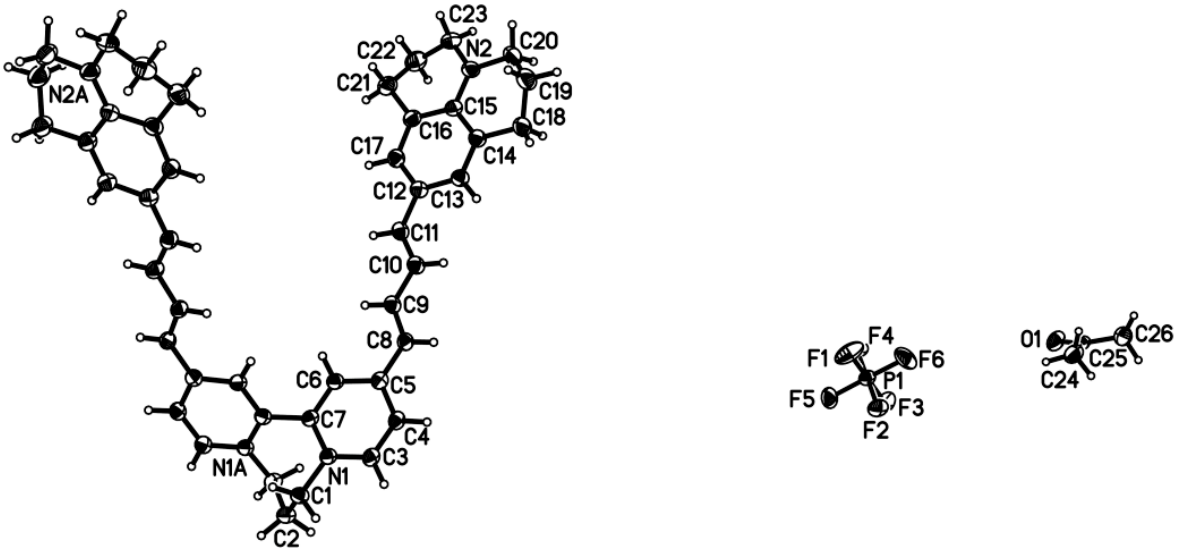

Figure S4. Representation of the molecular structure of [**18**][PF_6]$_2$•2Me_2CO (50% probability ellipsoids). While the dication has been completed by generating symmetry equivalent atoms, only the single PF_6^- anion and acetonitrile molecule in the asymmetric unit are shown.

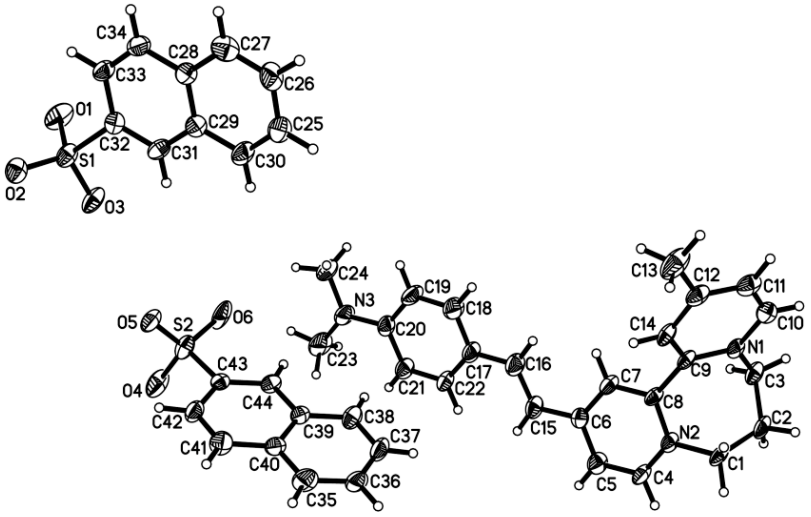

Figure S5. Representation of the molecular structure of [**7**][$NapSO_3$]$_2$ (50% probability ellipsoids).

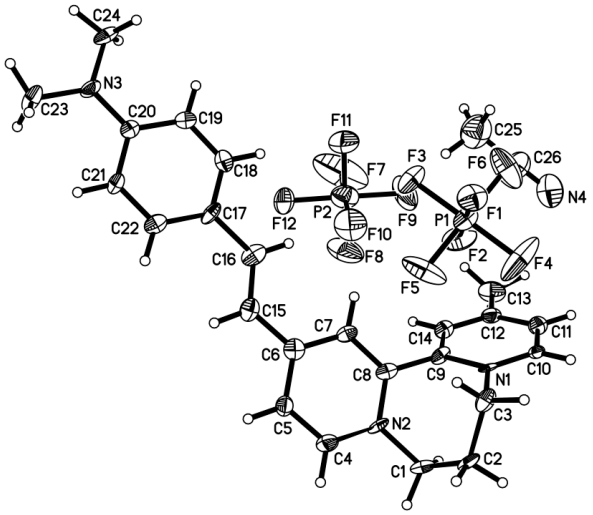

Figure S6. Representation of the molecular structure of [**7**][PF_6]$_2$•MeCN (50% probability ellipsoids).

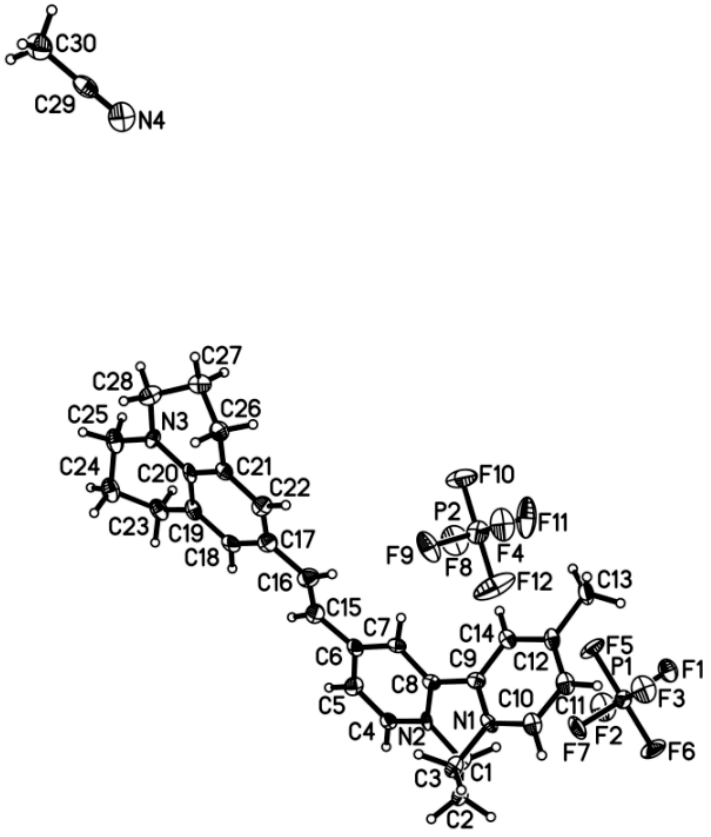

Figure S7. Representation of the molecular structure of [**9**][PF_6]$_2$•MeCN (50% probability ellipsoids).

4. Method for Derivation of β Components from HRS Data

The values of β_{zzz} and β_{zyy} can be determined from $\langle\beta^2_{HRS}\rangle$ and ρ as follows:

$$\begin{cases} \langle\beta^2_{HRS}\rangle = \langle\beta^2_{ZZZ}\rangle + \langle\beta^2_{YZZ}\rangle \\ \rho = \dfrac{\langle\beta^2_{ZZZ}\rangle}{\langle\beta^2_{YZZ}\rangle} \end{cases} \tag{1}$$

The HRS intensities with parallel polarization for fundamental and SH wavelengths, $\langle\beta^2_{ZZZ}\rangle$, and for perpendicular polarization, $\langle\beta^2_{YZZ}\rangle$, are given in terms of the molecular tensor components β_{zzz} and β_{zyy} according to

$$\begin{cases} \langle\beta^2_{ZZZ}\rangle = \dfrac{1}{7}\beta^2_{zzz} + \dfrac{6}{35}\beta_{zzz}\beta_{zyy} + \dfrac{9}{35}\beta^2_{zyy} \\ \langle\beta^2_{YZZ}\rangle = \dfrac{1}{35}\beta^2_{zzz} - \dfrac{2}{105}\beta_{zzz}\beta_{zyy} + \dfrac{11}{105}\beta^2_{zyy} \end{cases} \tag{2}$$

and ρ can be expressed in terms of the parameter $k = \beta_{zyy}/\beta_{zzz}$ by

$$\rho = \frac{15 + 18k + 27k^2}{3 - 2k + 11k^2} \tag{3}$$

It should be noted that the quadratic eq. 3 gives two solutions for k, and these lead to quite different values of the β components. Because both finite field/density functional theory and coupled perturbed Hartree Fock calculations predict that the β_{zyy} component dominates in DS diquat derivatives,[1] we have chosen to use the k values that afford results consistent with these theoretical methods. Due to the uncertainties in the depolarization measurements, all values of k are rounded to one significant figure. In cases where eq. 3 produces a solution of magnitude greater than 9, a value of 10 is used as an estimated upper limit for k; this approach stems from the nature of the mathematical relationship between k and ρ.[2]

One further point is worth making regarding these HRS data. Previous polarized HRS studies with the C_{2v} triarylmethane dyes Brilliant Green and Malachite Green indicate that ρ measurements can give misleading results due to Kleinman symmetry breaking.[3,4] This effect becomes important when using a SH wavelength to high energy of the ICT bands, and the importance of considering Kleinman-disallowed contributions has also been noted in studies with 2D Ni^{II} Schiff base complexes[5] and a Zn^{II} phthalocyanine derivative.[6] Because it is likely that a comparable situation may pertain for [**3**–**18**][PF_6]$_2$, the derived β_{zzz} and β_{zyy} values should be treated cautiously.

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5. Molecular Orbital Depictions (B3P86/6-31G*)

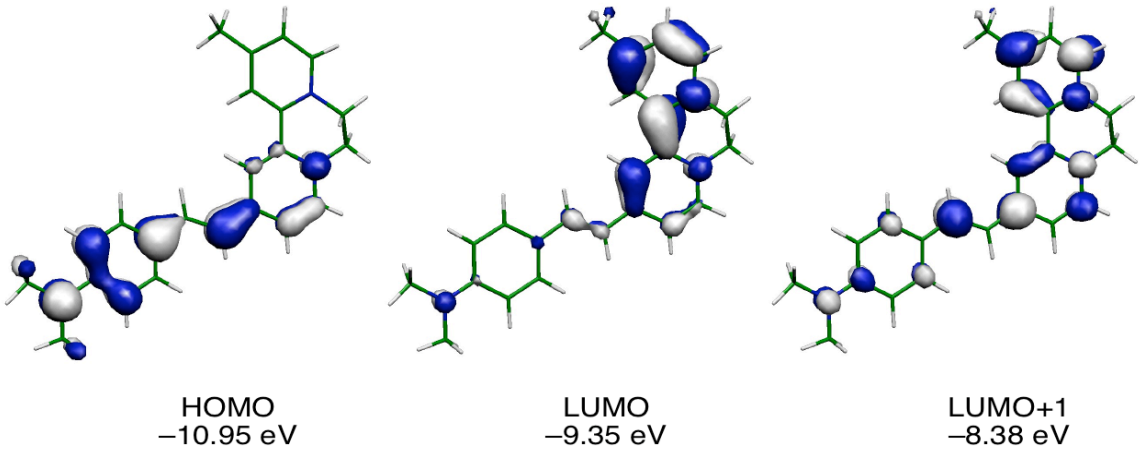

Figure S8. Illustrations of the contour surface diagrams of the molecular orbitals of **3** involved in the two lowest energy transitions (isosurface value 0.04 au). The axis convention for this and all subsequent Figures is as for Figure 10.

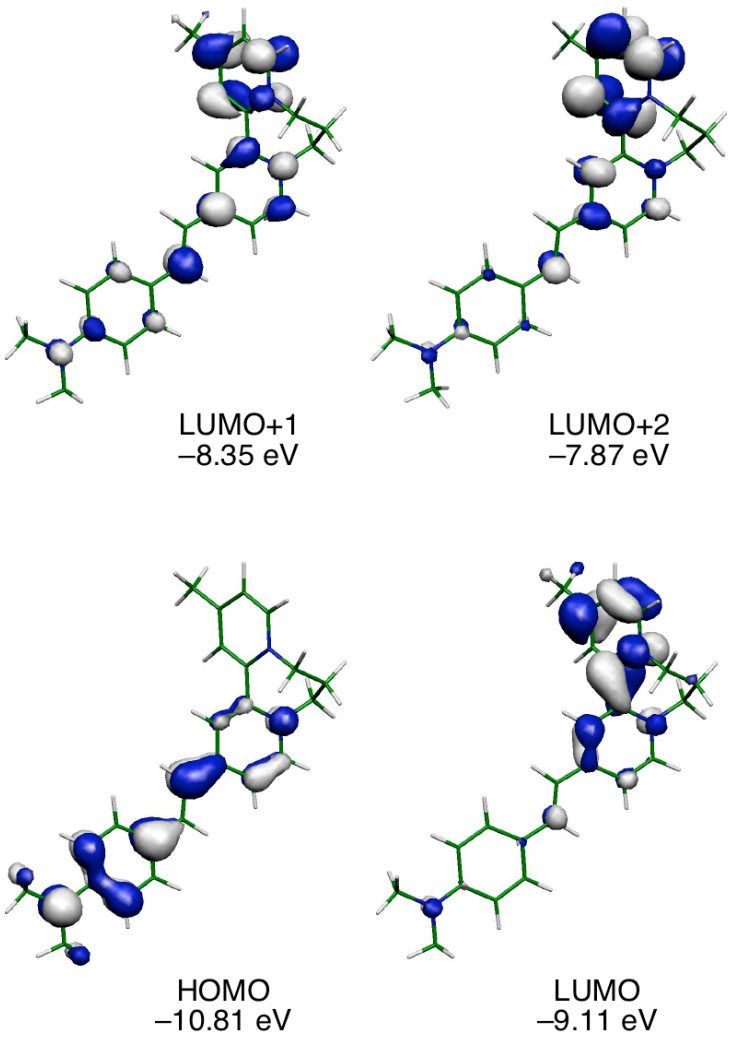

Figure S9. Illustrations of the contour surface diagrams of the molecular orbitals of **7** involved in the three lowest energy transitions (isosurface value 0.04 au).

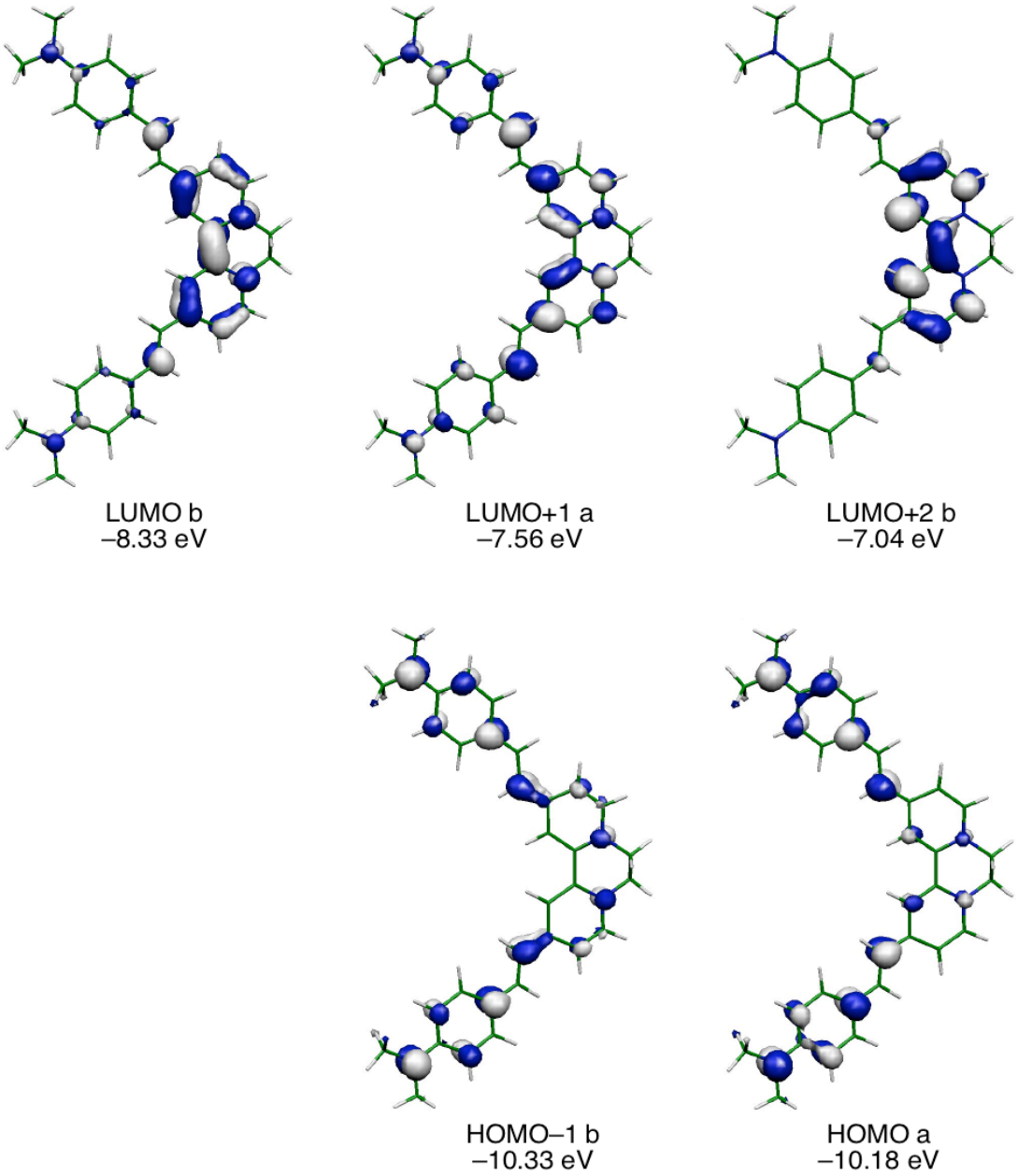

Figure S10. Illustrations of the contour surface diagrams of the molecular orbitals of **11** involved in the six lowest energy transitions (isosurface value 0.04 au).

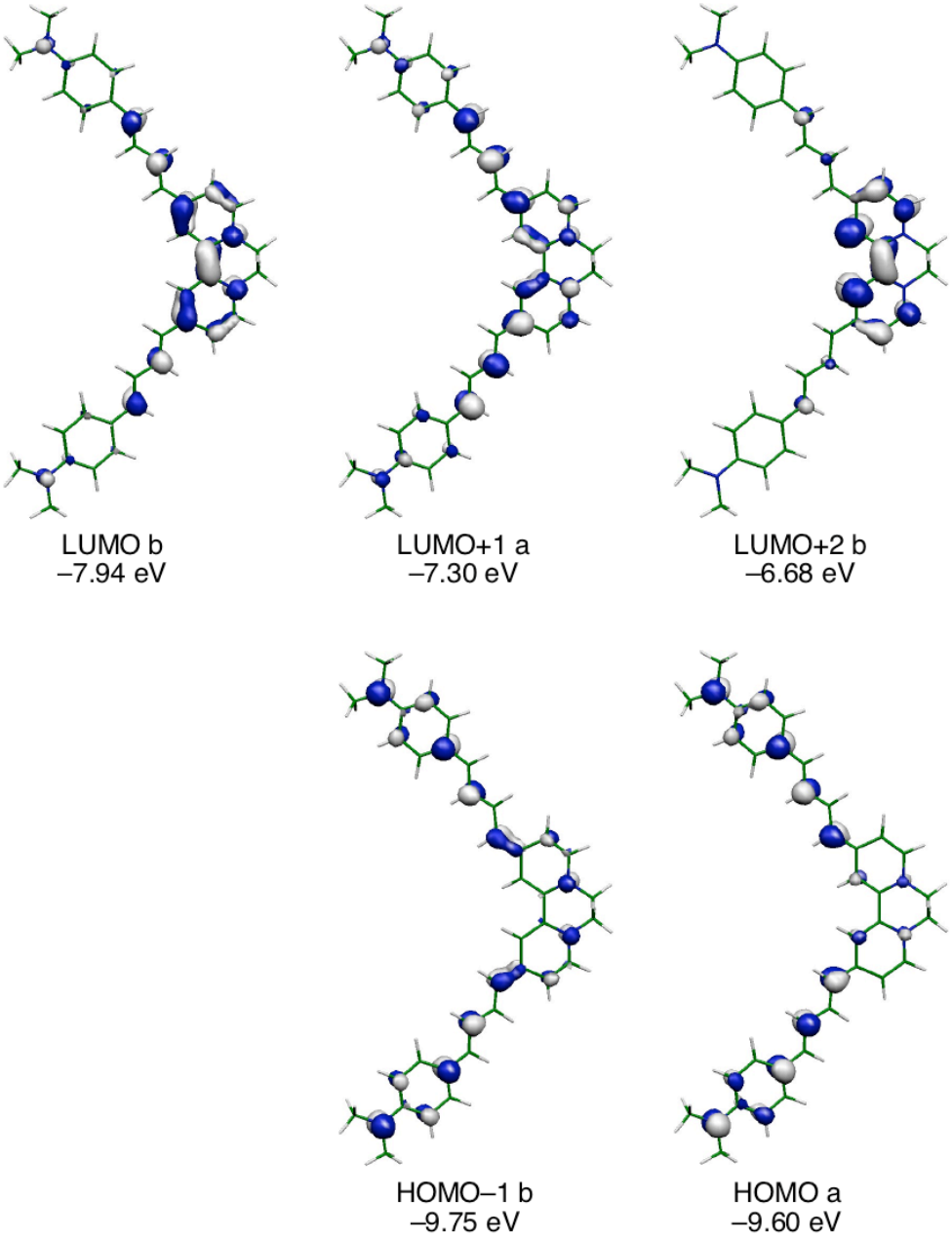

Figure S11. Illustrations of the contour surface diagrams of the molecular orbitals of **12** involved in the six lowest energy transitions (isosurface value 0.04 au).

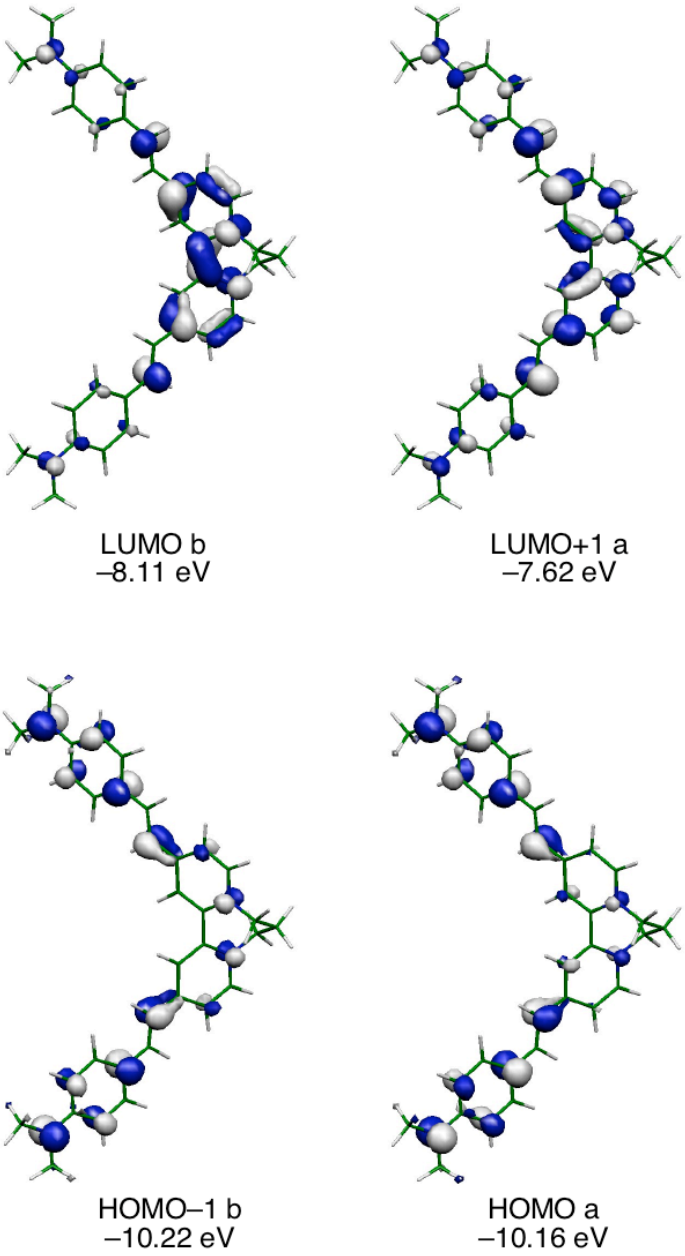

Figure S12. Illustrations of the contour surface diagrams of the molecular orbitals of **15** involved in the four lowest energy transitions (isosurface value 0.04 au).

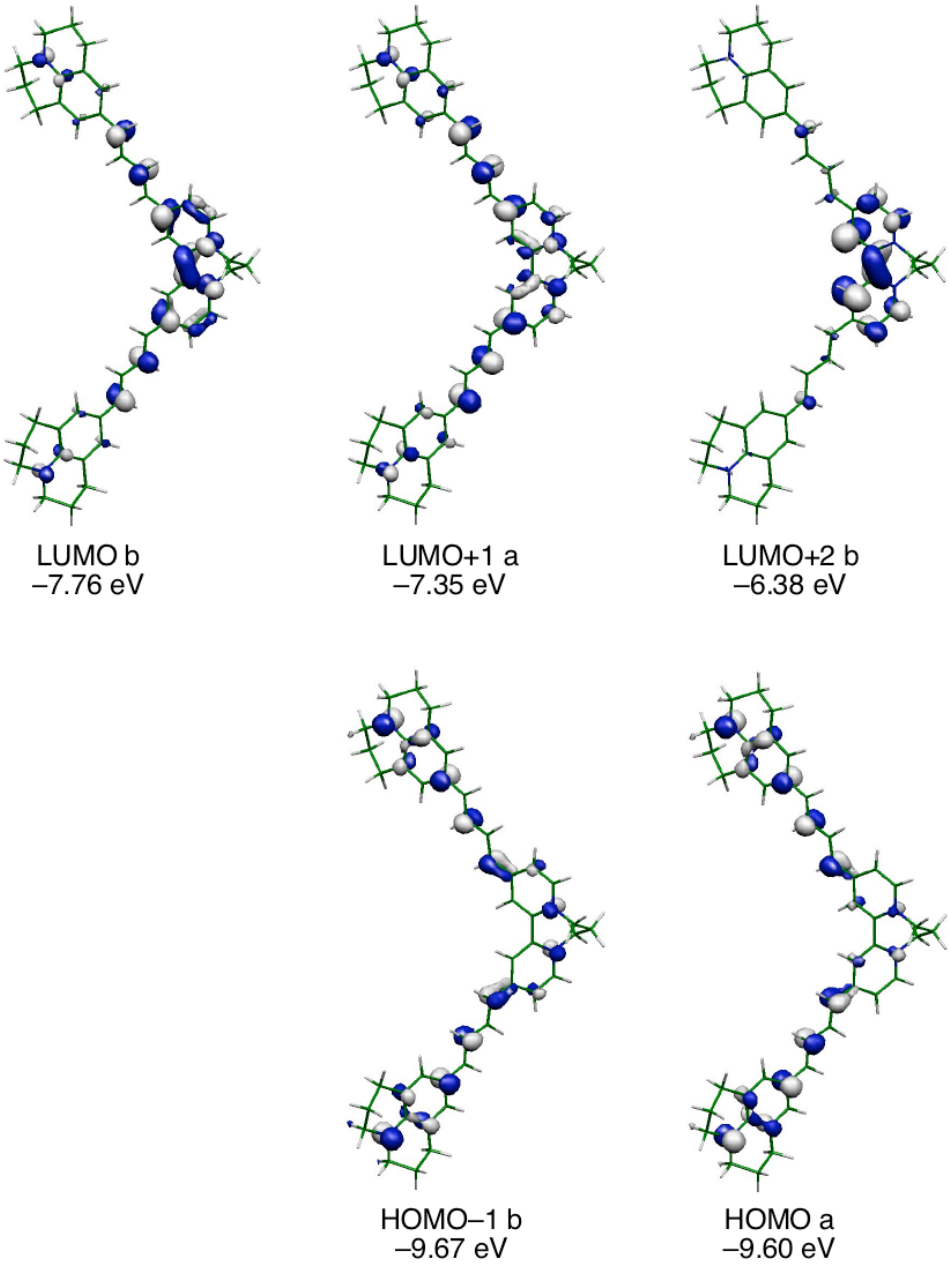

Figure S13. Illustrations of the contour surface diagrams of the molecular orbitals of **16** involved in the six lowest energy transitions (isosurface value 0.04 au).

6. Cartesian Coordinates of Theoretically-Optimized Geometries (B3P86/6-31G*)

Cation 3:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.883064	1.436990	0.211955
2	6	0	-3.536374	1.208431	0.177404
3	6	0	-5.806928	0.355421	0.072989
4	6	0	-5.266788	-0.959535	-0.101154
5	6	0	-3.918357	-1.168213	-0.130626
6	6	0	-2.989275	-0.095592	0.006927
7	7	0	-7.132629	0.561256	0.103958
8	6	0	-8.064819	-0.550233	-0.059531
9	6	0	-7.672660	1.902401	0.302646
10	6	0	-1.591646	-0.257873	-0.014894
11	6	0	-0.888761	-1.446669	-0.153652
12	6	0	0.507606	-1.595642	-0.169483
13	6	0	1.092002	-2.898218	-0.281946
14	6	0	1.448295	-0.524047	-0.072761
15	6	0	2.803921	-0.738505	-0.085509
16	7	0	3.303463	-2.020846	-0.160168
17	6	0	2.438016	-3.075031	-0.269573
18	6	0	3.767079	0.369224	-0.002547
19	7	0	5.028491	0.107873	0.448039
20	6	0	5.379426	-1.275107	0.822790
21	6	0	4.747163	-2.225771	-0.170936
22	6	0	3.455894	1.672920	-0.376959
23	6	0	4.380014	2.713202	-0.264500
24	6	0	5.655535	2.390066	0.230681
25	6	0	5.950611	1.092214	0.565781
26	6	0	4.045385	4.109797	-0.668976
27	1	0	-5.245794	2.448572	0.342189
28	1	0	-2.858008	2.051053	0.284696
29	1	0	-5.932408	-1.806627	-0.208212
30	1	0	-3.559365	-2.183479	-0.263336
31	1	0	-9.082807	-0.165816	-0.040585
32	1	0	-7.908426	-1.054521	-1.018397
33	1	0	-7.957502	-1.277130	0.752539
34	1	0	-8.759197	1.847653	0.332269
35	1	0	-7.326271	2.326809	1.250397
36	1	0	-7.384515	2.567850	-0.518058
37	1	0	-1.024652	0.665814	0.098568
38	1	0	-1.451611	-2.370299	-0.254941
39	1	0	0.455746	-3.772591	-0.362010
40	1	0	1.091712	0.491827	0.040958
41	1	0	2.897279	-4.054065	-0.342225
42	1	0	5.018621	-1.464437	1.839001
43	1	0	6.466272	-1.368918	0.809136
44	1	0	4.958925	-3.255944	0.121978
45	1	0	5.148265	-2.064042	-1.178914
46	1	0	2.477519	1.874189	-0.796616
47	1	0	6.424604	3.147869	0.336316
48	1	0	6.923980	0.790796	0.935485
49	1	0	4.736024	4.460069	-1.444608
50	1	0	3.026454	4.195596	-1.050375
51	1	0	4.156219	4.790417	0.183196

E(RB+HF-VWN+P86) = -1058.54851136 A.U.

Cation 7:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.925350	-0.998540	-0.236260
2	6	0	-4.619616	-1.388230	-0.337422
3	6	0	-6.256559	0.347000	0.109856
4	6	0	-5.175704	1.257654	0.342069
5	6	0	-3.876885	0.850105	0.234494
6	6	0	-3.537726	-0.490190	-0.109834
7	7	0	-7.534510	0.745240	0.215106
8	6	0	-7.860478	2.118971	0.582885
9	6	0	-8.626396	-0.190305	-0.034259
10	6	0	-2.220373	-0.966768	-0.234697
11	6	0	-1.036950	-0.258824	-0.068242
12	6	0	0.249757	-0.800870	-0.213313
13	6	0	0.552566	-2.166259	-0.520129
14	6	0	1.398647	0.036058	-0.048235
15	6	0	2.678174	-0.434793	-0.179011
16	7	0	2.910459	-1.757416	-0.495280
17	6	0	1.837402	-2.591414	-0.650688
18	6	0	3.830304	0.474002	0.004900
19	7	0	4.858266	0.110304	0.828076
20	6	0	4.801486	-1.185920	1.542322
21	6	0	4.278525	-2.239133	-0.703681
22	6	0	3.879039	1.708485	-0.628363
23	6	0	4.952456	2.588420	-0.447041
24	6	0	5.990265	2.159956	0.394468
25	6	0	5.916359	0.931913	1.010096
26	6	0	5.006167	3.915221	-1.126918
27	1	0	-6.709044	-1.722394	-0.419134
28	1	0	-4.397632	-2.419065	-0.601152
29	1	0	-5.384887	2.286654	0.605780
30	1	0	-3.091903	1.576355	0.420106
31	1	0	-8.942413	2.226012	0.633680
32	1	0	-7.446259	2.371484	1.564385
33	1	0	-7.481372	2.826909	-0.161725
34	1	0	-9.574967	0.331410	0.078417
35	1	0	-8.574947	-0.590141	-1.052170
36	1	0	-8.604142	-1.020266	0.679911
37	1	0	-2.144328	-2.020515	-0.498717
38	1	0	-1.086558	0.797070	0.183989
39	1	0	-0.233254	-2.898257	-0.658839
40	1	0	1.257675	1.078969	0.217277
41	1	0	2.078979	-3.619171	-0.896037
42	1	0	3.068169	1.970551	-1.299345
43	1	0	6.859835	2.783584	0.573791
44	1	0	6.691942	0.569053	1.674673
45	1	0	5.912221	3.997676	-1.737926
46	1	0	4.139545	4.084555	-1.768189
47	1	0	5.051577	4.721124	-0.385047
48	6	0	5.054082	-2.365992	0.607804
49	1	0	4.778512	-1.547110	-1.389320
50	1	0	4.226045	-3.201377	-1.215471
51	1	0	4.764388	-3.274548	1.145801
52	1	0	6.119838	-2.457932	0.373941
53	1	0	3.812193	-1.247977	2.003407
54	1	0	5.536143	-1.152830	2.347810

E(RB+HF-VWN+P86) = -1098.01125666 A.U.

Cation 11:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.902450	1.884248	-0.218915
2	6	0	3.457287	3.148221	-0.589515
3	6	0	1.497755	1.891641	0.018116
4	6	0	0.727731	3.022198	-0.109924
5	7	0	1.328733	4.215065	-0.442193
6	6	0	2.671730	4.253765	-0.681263
7	6	0	-0.727731	3.022198	0.109924
8	6	0	-1.497755	1.891641	-0.018115
9	6	0	-2.902450	1.884248	0.218916
10	6	0	-3.457287	3.148221	0.589515
11	6	0	-2.671730	4.253765	0.681263
12	7	0	-1.328733	4.215065	0.442193
13	6	0	0.513860	5.423157	-0.556115
14	6	0	-0.513860	5.423157	0.556115
15	6	0	-3.636890	0.689771	0.065286
16	6	0	-4.998124	0.567475	0.272960
17	6	0	-5.802101	-0.584977	0.129749
18	6	0	-5.313885	-1.856048	-0.277561
19	6	0	-6.141250	-2.938002	-0.404853
20	6	0	-7.540129	-2.832480	-0.130795
21	6	0	-8.037466	-1.560916	0.278335
22	6	0	-7.193686	-0.489765	0.399532
23	7	0	-8.357024	-3.896247	-0.255289
24	6	0	-9.781377	-3.769691	0.024319
25	6	0	-7.835034	-5.188810	-0.677604
26	6	0	3.636890	0.689772	-0.065286
27	6	0	4.998124	0.567475	-0.272960
28	6	0	5.802101	-0.584977	-0.129749
29	6	0	7.193686	-0.489765	-0.399533
30	6	0	8.037466	-1.560916	-0.278336
31	6	0	7.540129	-2.832480	0.130795
32	6	0	6.141250	-2.938001	0.404854
33	6	0	5.313885	-1.856048	0.277562
34	7	0	8.357025	-3.896247	0.255289
35	6	0	7.835034	-5.188809	0.677605
36	6	0	9.781377	-3.769691	-0.024320
37	1	0	4.515386	3.264355	-0.787197
38	1	0	1.019821	0.973243	0.339093
39	1	0	3.070917	5.225749	-0.947106
40	1	0	-1.019821	0.973243	-0.339093
41	1	0	-4.515386	3.264355	0.787197
42	1	0	-3.070917	5.225749	0.947106
43	1	0	0.026030	5.453988	-1.537422
44	1	0	1.167158	6.292955	-0.465229
45	1	0	-1.167158	6.292955	0.465229
46	1	0	-0.026030	5.453988	1.537422
47	1	0	-3.067950	-0.184224	-0.240855
48	1	0	-5.542998	1.456739	0.586789
49	1	0	-4.259032	-1.984645	-0.499540
50	1	0	-5.723214	-3.885667	-0.720345
51	1	0	-9.089852	-1.431590	0.496558
52	1	0	-7.602560	0.467566	0.712741
53	1	0	-10.262463	-4.734006	-0.130453
54	1	0	-9.954216	-3.464397	1.062022
55	1	0	-10.252533	-3.041790	-0.645203
56	1	0	-8.650922	-5.908961	-0.709053
57	1	0	-7.393745	-5.130156	-1.678654
58	1	0	-7.080713	-5.559612	0.024919
59	1	0	3.067950	-0.184224	0.240855
60	1	0	5.542998	1.456739	-0.586790
61	1	0	7.602560	0.467565	-0.712742
62	1	0	9.089851	-1.431591	-0.496559

63	1	0	5.723214	-3.885667	0.720346
64	1	0	4.259032	-1.984645	0.499542
65	1	0	8.650922	-5.908961	0.709053
66	1	0	7.393745	-5.130155	1.678654
67	1	0	7.080713	-5.559612	-0.024918
68	1	0	10.262463	-4.734006	0.130453
69	1	0	9.954215	-3.464398	-1.062023
70	1	0	10.252533	-3.041790	0.645201

E(RB+HF-VWN+P86) = -1462.96771917 A.U.

Cation 12:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.188396	-2.903848	2.479491
2	6	0	0.543656	-3.466194	3.747272
3	6	0	-0.031344	-1.495431	2.488358
4	6	0	0.101048	-0.728359	3.619302
5	7	0	0.420748	-1.335455	4.814947
6	6	0	0.640676	-2.683489	4.852714
7	6	0	-0.101048	0.728359	3.619302
8	6	0	0.031344	1.495431	2.488358
9	6	0	-0.188396	2.903848	2.479491
10	6	0	-0.543656	3.466194	3.747272
11	6	0	-0.640676	2.683489	4.852714
12	7	0	-0.420748	1.335455	4.814947
13	6	0	0.547551	-0.523228	6.021462
14	6	0	-0.547551	0.523228	6.021462
15	6	0	-0.056213	5.713225	-0.042253
16	6	0	-0.253148	7.083996	-0.099290
17	6	0	-0.122736	7.944158	-1.211766
18	6	0	0.253148	7.510941	-2.511539
19	6	0	0.368308	8.386368	-3.557376
20	6	0	0.112808	9.780364	-3.381826
21	6	0	-0.264811	10.222765	-2.081402
22	6	0	-0.374550	9.331809	-1.046747
23	7	0	0.225542	10.645582	-4.410720
24	6	0	-0.038933	12.063581	-4.213389
25	6	0	0.615594	10.178273	-5.732798
26	6	0	0.056213	-5.713225	-0.042253
27	6	0	0.253148	-7.083996	-0.099290
28	6	0	0.122736	-7.944158	-1.211766
29	6	0	0.374550	-9.331809	-1.046747
30	6	0	0.264811	-10.222765	-2.081402
31	6	0	-0.112808	-9.780364	-3.381826
32	6	0	-0.368308	-8.386368	-3.557376
33	6	0	-0.253148	-7.510941	-2.511539
34	7	0	-0.225542	-10.645582	-4.410720
35	6	0	-0.615594	-10.178273	-5.732798
36	6	0	0.038933	-12.063581	-4.213389
37	1	0	0.725740	-4.527473	3.860934
38	1	0	-0.342307	-1.013268	1.568767
39	1	0	0.896359	-3.086263	5.825954
40	1	0	0.342307	1.013268	1.568767
41	1	0	-0.725740	4.527473	3.860934
42	1	0	-0.896359	3.086263	5.825954
43	1	0	1.535965	-0.049516	6.054082
44	1	0	0.446016	-1.174818	6.891542
45	1	0	-0.446016	1.174818	6.891542
46	1	0	-1.535965	0.049516	6.054082
47	1	0	0.235017	5.162811	-0.934041
48	1	0	-0.545627	7.568093	0.833385
49	1	0	0.458212	6.460300	-2.691993

50	1	0	0.658554	8.008172	-4.529599
51	1	0	-0.467965	11.270494	-1.899517
52	1	0	-0.663889	9.698226	-0.065109
53	1	0	0.101173	12.587448	-5.157606
54	1	0	-1.068951	12.231361	-3.879760
55	1	0	0.648021	12.496423	-3.477649
56	1	0	0.648068	11.026299	-6.415018
57	1	0	1.609984	9.718391	-5.714015
58	1	0	-0.105120	9.452529	-6.125810
59	1	0	-0.235017	-5.162811	-0.934041
60	1	0	0.545627	-7.568093	0.833385
61	1	0	0.663889	-9.698226	-0.065109
62	1	0	0.467965	-11.270494	-1.899517
63	1	0	-0.658554	-8.008172	-4.529599
64	1	0	-0.458212	-6.460300	-2.691993
65	1	0	-0.648068	-11.026299	-6.415018
66	1	0	-1.609984	-9.718391	-5.714015
67	1	0	0.105120	-9.452529	-6.125810
68	1	0	-0.101173	-12.587448	-5.157606
69	1	0	1.068951	-12.231361	-3.879760
70	1	0	-0.648021	-12.496423	-3.477649
71	6	0	0.036034	-3.633550	1.287868
72	6	0	0.219036	-5.002800	1.148783
73	1	0	-0.251964	-3.069451	0.403032
74	1	0	0.510176	-5.586552	2.021642
75	6	0	-0.036034	3.633550	1.287868
76	6	0	-0.219036	5.002800	1.148783
77	1	0	0.251964	3.069451	0.403032
78	1	0	-0.510176	5.586552	2.021642

E(RB+HF-VWN+P86) = -1618.29892289 A.U.

Cation 14:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.232151	-2.901174	3.105558
2	6	0	0.596524	-3.457842	4.374959
3	6	0	-0.008706	-1.495686	3.115334
4	6	0	0.112035	-0.726333	4.245572
5	7	0	0.440640	-1.328651	5.442602
6	6	0	0.681215	-2.674122	5.479639
7	6	0	-0.112035	0.726333	4.245572
8	6	0	0.008706	1.495686	3.115334
9	6	0	-0.232151	2.901174	3.105558
10	6	0	-0.596524	3.457842	4.374959
11	6	0	-0.681215	2.674122	5.479639
12	7	0	-0.440640	1.328651	5.442602
13	6	0	0.555366	-0.515154	6.648206
14	6	0	-0.555366	0.515154	6.648206
15	6	0	-0.138290	5.715309	0.589654
16	6	0	-0.358345	7.084836	0.530476
17	6	0	-0.232151	7.945945	-0.578254
18	6	0	0.164703	7.520054	-1.872616
19	6	0	0.285858	8.385419	-2.927876
20	6	0	0.024166	9.785062	-2.727580
21	6	0	-0.404040	10.236866	-1.435817
22	6	0	-0.508099	9.327874	-0.414654
23	7	0	0.185168	10.663808	-3.743418
24	6	0	-0.147273	12.081074	-3.598715
25	6	0	0.550171	10.232758	-5.092119
26	6	0	0.138290	-5.715309	0.589654
27	6	0	0.358345	-7.084836	0.530476
28	6	0	0.232151	-7.945945	-0.578254

29	6	0	0.508099	-9.327874	-0.414654
30	6	0	0.404040	-10.236866	-1.435817
31	6	0	-0.024166	-9.785062	-2.727580
32	6	0	-0.285858	-8.385419	-2.927876
33	6	0	-0.164703	-7.520054	-1.872616
34	7	0	-0.185168	-10.663808	-3.743418
35	6	0	-0.550171	-10.232758	-5.092119
36	6	0	0.147273	-12.081074	-3.598715
37	1	0	0.794134	-4.516348	4.488486
38	1	0	-0.327244	-1.017943	2.195969
39	1	0	0.942671	-3.072728	6.453086
40	1	0	0.327244	1.017943	2.195969
41	1	0	-0.794134	4.516348	4.488486
42	1	0	-0.942671	3.072728	6.453086
43	1	0	1.536083	-0.025430	6.681921
44	1	0	0.463723	-1.168219	7.518397
45	1	0	-0.463723	1.168219	7.518397
46	1	0	-1.536083	0.025430	6.681921
47	1	0	0.168285	5.171294	-0.301049
48	1	0	-0.667145	7.562822	1.461080
49	1	0	0.381583	6.469804	-2.048334
50	1	0	-0.819394	9.682669	0.565849
51	1	0	-1.187696	12.243491	-3.917003
52	1	0	0.490718	12.637942	-4.291302
53	1	0	-0.364698	10.069547	-5.681036
54	1	0	1.091820	11.058303	-5.563229
55	1	0	-0.168285	-5.171294	-0.301049
56	1	0	0.667145	-7.562822	1.461080
57	1	0	0.819394	-9.682669	0.565849
58	1	0	-0.381583	-6.469804	-2.048334
59	1	0	0.364698	-10.069547	-5.681036
60	1	0	-1.091820	-11.058303	-5.563229
61	1	0	1.187696	-12.243491	-3.917003
62	1	0	-0.490718	-12.637942	-4.291302
63	6	0	0.089666	-3.633363	1.916485
64	6	0	0.295086	-5.001365	1.776929
65	1	0	-0.209886	-3.075109	1.031632
66	1	0	0.600535	-5.578434	2.649415
67	6	0	-0.089666	3.633363	1.916485
68	6	0	-0.295086	5.001365	1.776929
69	1	0	0.209886	3.075109	1.031632
70	1	0	-0.600535	5.578434	2.649415
71	6	0	0.057442	12.567664	-2.176124
72	6	0	-0.737217	11.689468	-1.221262
73	1	0	-0.259835	13.612117	-2.105689
74	1	0	1.124316	12.531029	-1.927263
75	1	0	-0.543671	11.966748	-0.180049
76	1	0	-1.811641	11.848899	-1.390663
77	6	0	-0.057442	-12.567664	-2.176124
78	6	0	0.737217	-11.689468	-1.221262
79	1	0	0.259835	-13.612117	-2.105689
80	1	0	-1.124316	-12.531029	-1.927263
81	1	0	0.543671	-11.966748	-0.180049
82	1	0	1.811641	-11.848899	-1.390663
83	6	0	1.402280	8.977748	-5.072809
84	6	0	0.678354	7.889390	-4.294438
85	1	0	2.369494	9.199184	-4.607028
86	1	0	1.597962	8.661608	-6.101602
87	1	0	1.299691	6.992789	-4.201137
88	1	0	-0.222731	7.588810	-4.848024
89	6	0	-1.402280	-8.977748	-5.072809
90	6	0	-0.678354	-7.889390	-4.294438
91	1	0	-2.369494	-9.199184	-4.607028
92	1	0	-1.597962	-8.661608	-6.101602
93	1	0	-1.299691	-6.992789	-4.201137
94	1	0	0.222731	-7.588810	-4.848024

E(RB+HF-VWN+P86) = -1929.07131229 A.U.

Cation 15:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.459518	-2.886446	1.585745
2	6	0	1.189179	-3.296773	2.742124
3	6	0	0.000000	-1.535267	1.620431
4	6	0	0.243493	-0.699061	2.679292
5	7	0	0.961488	-1.149232	3.765528
6	6	0	1.412054	-2.436431	3.773600
7	6	0	-0.243493	0.699061	2.679292
8	6	0	0.000000	1.535267	1.620431
9	6	0	-0.459518	2.886446	1.585745
10	6	0	-1.189179	3.296773	2.742124
11	6	0	-1.412054	2.436431	3.773600
12	7	0	-0.961488	1.149232	3.765528
13	6	0	1.240509	-0.249641	4.891262
14	6	0	-1.240509	0.249641	4.891262
15	6	0	-0.166984	3.703102	0.473828
16	6	0	-0.560640	5.021091	0.336462
17	6	0	-0.297716	5.902212	-0.735827
18	6	0	0.456919	5.555920	-1.889194
19	6	0	0.682919	6.452314	-2.897761
20	6	0	0.164293	7.782385	-2.831463
21	6	0	-0.592038	8.137911	-1.676981
22	6	0	-0.806972	7.226944	-0.677817
23	7	0	0.382590	8.666608	-3.824152
24	6	0	-0.151252	10.019353	-3.737597
25	6	0	1.154907	8.288542	-4.999774
26	6	0	0.166984	-3.703102	0.473828
27	6	0	0.560640	-5.021091	0.336462
28	6	0	0.297716	-5.902212	-0.735827
29	6	0	0.806972	-7.226944	-0.677817
30	6	0	0.592038	-8.137911	-1.676981
31	6	0	-0.164293	-7.782385	-2.831463
32	6	0	-0.682919	-6.452314	-2.897761
33	6	0	-0.456919	-5.555920	-1.889194
34	7	0	-0.382590	-8.666608	-3.824152
35	6	0	-1.154907	-8.288542	-4.999774
36	6	0	0.151252	-10.019353	-3.737597
37	1	0	1.582819	-4.301477	2.833054
38	1	0	-0.589542	-1.152506	0.794008
39	1	0	1.969073	-2.730687	4.655599
40	1	0	0.589542	1.152506	0.794008
41	1	0	-1.582819	4.301477	2.833054
42	1	0	-1.969073	2.730687	4.655599
43	1	0	1.624720	0.688218	4.478920
44	1	0	2.043925	-0.690276	5.483773
45	1	0	-2.043925	0.690276	5.483773
46	1	0	-1.624720	-0.688218	4.478920
47	1	0	0.413250	3.238960	-0.319339
48	1	0	-1.148240	5.458823	1.142374
49	1	0	0.873112	4.557727	-1.984018
50	1	0	1.265996	6.142415	-3.755907
51	1	0	-1.003927	9.134384	-1.580532
52	1	0	-1.387993	7.527711	0.190369
53	1	0	0.130264	10.571839	-4.632463
54	1	0	-1.244748	10.009044	-3.672743
55	1	0	0.252876	10.549011	-2.867968
56	1	0	1.204333	9.136616	-5.680644
57	1	0	2.179089	8.008932	-4.729117
58	1	0	0.684605	7.453243	-5.530010
59	1	0	-0.413250	-3.238960	-0.319339
60	1	0	1.148240	-5.458823	1.142374
61	1	0	1.387993	-7.527711	0.190369
62	1	0	1.003927	-9.134384	-1.580532

63	1	0	-1.265996	-6.142415	-3.755907
64	1	0	-0.873112	-4.557727	-1.984018
65	1	0	-1.204333	-9.136616	-5.680644
66	1	0	-2.179089	-8.008932	-4.729117
67	1	0	-0.684605	-7.453243	-5.530010
68	1	0	-0.130264	-10.571839	-4.632463
69	1	0	1.244748	-10.009044	-3.672743
70	1	0	-0.252876	-10.549011	-2.867968
71	6	0	0.000000	0.000000	5.749229
72	1	0	-0.202823	-0.857567	6.399355
73	1	0	0.202823	0.857567	6.399355

E(RB+HF-VWN+P86) = -1502.42815485 A.U.

Cation 16:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.423675	-2.888410	2.195552
2	6	0	1.137783	-3.316566	3.358079
3	6	0	-0.017819	-1.530131	2.235579
4	6	0	0.232182	-0.702255	3.298082
5	7	0	0.938333	-1.168216	4.388037
6	6	0	1.366562	-2.464814	4.393686
7	6	0	-0.232182	0.702255	3.298082
8	6	0	0.017819	1.530131	2.235579
9	6	0	-0.423675	2.888410	2.195552
10	6	0	-1.137783	3.316566	3.358079
11	6	0	-1.366562	2.464814	4.393686
12	7	0	-0.938333	1.168216	4.388037
13	6	0	1.234420	-0.275377	5.512611
14	6	0	-1.234420	0.275377	5.512611
15	6	0	-0.203389	5.802200	-0.197389
16	6	0	-0.615181	7.122026	-0.290684
17	6	0	-0.387441	8.039562	-1.340273
18	6	0	0.350771	7.734539	-2.514948
19	6	0	0.541852	8.658967	-3.506292
20	6	0	0.000000	9.975587	-3.398886
21	6	0	-0.738563	10.290492	-2.222340
22	6	0	-0.917581	9.352688	-1.239788
23	7	0	0.181209	10.887149	-4.377078
24	6	0	-0.386389	12.221946	-4.254053
25	6	0	0.945053	10.551953	-5.569734
26	6	0	0.203389	-5.802200	-0.197389
27	6	0	0.615181	-7.122026	-0.290684
28	6	0	0.387441	-8.039562	-1.340273
29	6	0	0.917581	-9.352688	-1.239788
30	6	0	0.738563	-10.290492	-2.222340
31	6	0	0.000000	-9.975587	-3.398886
32	6	0	-0.541852	-8.658967	-3.506292
33	6	0	-0.350771	-7.734539	-2.514948
34	7	0	-0.181209	-10.887149	-4.377078
35	6	0	-0.945053	-10.551953	-5.569734
36	6	0	0.386389	-12.221946	-4.254053
37	1	0	1.512824	-4.328792	3.445649
38	1	0	-0.597886	-1.135985	1.407874
39	1	0	1.911835	-2.771077	5.278971
40	1	0	0.597886	1.135985	1.407874
41	1	0	-1.512824	4.328792	3.445649
42	1	0	-1.911835	2.771077	5.278971
43	1	0	1.636596	0.655589	5.101404
44	1	0	2.029193	-0.731482	6.105282
45	1	0	-2.029193	0.731482	6.105282
46	1	0	-1.636596	-0.655589	5.101404

47	1	0	0.370610	5.348601	-1.002291
48	1	0	-1.191786	7.508318	0.550835
49	1	0	0.781432	6.745972	-2.640361
50	1	0	1.112813	8.379087	-4.382747
51	1	0	-1.164525	11.277482	-2.093841
52	1	0	-1.485670	9.621545	-0.352864
53	1	0	-0.151844	12.793630	-5.150619
54	1	0	-1.476379	12.179529	-4.152350
55	1	0	0.030592	12.752994	-3.390911
56	1	0	0.978588	11.419650	-6.226731
57	1	0	1.975139	10.276523	-5.317428
58	1	0	0.480419	9.725710	-6.119468
59	1	0	-0.370610	-5.348601	-1.002291
60	1	0	1.191786	-7.508318	0.550835
61	1	0	1.485670	-9.621545	-0.352864
62	1	0	1.164525	-11.277482	-2.093841
63	1	0	-1.112813	-8.379087	-4.382747
64	1	0	-0.781432	-6.745972	-2.640361
65	1	0	-0.978588	-11.419650	-6.226731
66	1	0	-1.975139	-10.276523	-5.317428
67	1	0	-0.480419	-9.725710	-6.119468
68	1	0	0.151844	-12.793630	-5.150619
69	1	0	1.476379	-12.179529	-4.152350
70	1	0	-0.030592	-12.752994	-3.390911
71	6	0	0.000000	0.000000	6.371570
72	1	0	-0.219981	-0.853605	7.021483
73	1	0	0.219981	0.853605	7.021483
74	6	0	0.133694	-3.691763	1.079923
75	6	0	0.507508	-5.019193	0.918034
76	1	0	-0.432975	-3.224982	0.276740
77	1	0	1.081268	-5.504950	1.706985
78	6	0	-0.133694	3.691763	1.079923
79	6	0	-0.507508	5.019193	0.918034
80	1	0	0.432975	3.224982	0.276740
81	1	0	-1.081268	5.504950	1.706985

E(RB+HF-VWN+P86) = -1657.75876636 A.U.

Cation 18:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.456385	-2.883962	2.793453
2	6	0	1.177013	-3.303341	3.957031
3	6	0	0.000000	-1.529829	2.834396
4	6	0	0.240188	-0.699235	3.896240
5	7	0	0.951871	-1.157086	4.987521
6	6	0	1.395407	-2.449601	4.992186
7	6	0	-0.240188	0.699235	3.896240
8	6	0	0.000000	1.529829	2.834396
9	6	0	-0.456385	2.883962	2.793453
10	6	0	-1.177013	3.303341	3.957031
11	6	0	-1.395407	2.449601	4.992186
12	7	0	-0.951871	1.157086	4.987521
13	6	0	1.237159	-0.261124	6.111005
14	6	0	-1.237159	0.261124	6.111005
15	6	0	-0.253527	5.800333	0.405438
16	6	0	-0.672312	7.119966	0.303848
17	6	0	-0.432390	8.034454	-0.741899
18	6	0	0.325473	7.728814	-1.902062
19	6	0	0.547729	8.641844	-2.899150
20	6	0	0.015801	9.971105	-2.771109
21	6	0	-0.774934	10.297834	-1.620668
22	6	0	-0.964959	9.346091	-0.651864

23	7	0	0.263312	10.902315	-3.721234
24	6	0	-0.320183	12.242437	-3.660568
25	6	0	0.998747	10.584631	-4.944491
26	6	0	0.253527	-5.800333	0.405438
27	6	0	0.672312	-7.119966	0.303848
28	6	0	0.432390	-8.034454	-0.741899
29	6	0	0.964959	-9.346091	-0.651864
30	6	0	0.774934	-10.297834	-1.620668
31	6	0	-0.015801	-9.971105	-2.771109
32	6	0	-0.547729	-8.641844	-2.899150
33	6	0	-0.325473	-7.728814	-1.902062
34	7	0	-0.263312	-10.902315	-3.721234
35	6	0	-0.998747	-10.584631	-4.944491
36	6	0	0.320183	-12.242437	-3.660568
37	1	0	1.563538	-4.311304	4.044153
38	1	0	-0.584964	-1.141979	2.007144
39	1	0	1.943861	-2.749549	5.877699
40	1	0	0.584964	1.141979	2.007144
41	1	0	-1.563538	4.311304	4.044153
42	1	0	-1.943861	2.749549	5.877699
43	1	0	1.627387	0.675201	5.700169
44	1	0	2.037681	-0.707178	6.703761
45	1	0	-2.037681	0.707178	6.703761
46	1	0	-1.627387	-0.675201	5.700169
47	1	0	0.332070	5.350648	-0.393410
48	1	0	-1.262247	7.504283	1.137004
49	1	0	0.751185	6.735770	-2.018162
50	1	0	-1.554688	9.608246	0.224351
51	1	0	-1.267128	12.251071	-4.220389
52	1	0	0.365080	12.919973	-4.178565
53	1	0	0.287093	10.292670	-5.731083
54	1	0	1.487710	11.504039	-5.279776
55	1	0	-0.332070	-5.350648	-0.393410
56	1	0	1.262247	-7.504283	1.137004
57	1	0	1.554688	-9.608246	0.224351
58	1	0	-0.751185	-6.735770	-2.018162
59	1	0	-0.287093	-10.292670	-5.731083
60	1	0	-1.487710	-11.504039	-5.279776
61	1	0	1.267128	-12.251071	-4.220389
62	1	0	-0.365080	-12.919973	-4.178565
63	6	0	0.000000	0.000000	6.970722
64	1	0	-0.209599	-0.856399	7.620490
65	1	0	0.209599	0.856399	7.620490
66	6	0	0.172932	-3.690305	1.681059
67	6	0	0.559388	-5.016113	1.516666
68	1	0	-0.401891	-3.230551	0.879451
69	1	0	1.143081	-5.495565	2.302246
70	6	0	-0.172932	3.690305	1.681059
71	6	0	-0.559388	5.016113	1.516666
72	1	0	0.401891	3.230551	0.879451
73	1	0	-1.143081	5.495565	2.302246
74	6	0	-0.542093	12.698666	-2.230612
75	6	0	-1.386005	11.668146	-1.495615
76	1	0	-1.033755	13.675765	-2.238888
77	1	0	0.426122	12.822194	-1.731840
78	1	0	-1.496112	11.932255	-0.438954
79	1	0	-2.399512	11.659049	-1.921340
80	6	0	0.542093	-12.698666	-2.230612
81	6	0	1.386005	-11.668146	-1.495615
82	1	0	1.033755	-13.675765	-2.238888
83	1	0	-0.426122	-12.822194	-1.731840
84	1	0	1.496112	-11.932255	-0.438954
85	1	0	2.399512	-11.659049	-1.921340
86	6	0	2.022329	9.487705	-4.718812
87	6	0	1.331922	8.267191	-4.128935
88	1	0	2.802135	9.849718	-4.038801
89	1	0	2.503751	9.245336	-5.670747
90	1	0	2.057972	7.485202	-3.883845
91	1	0	0.653325	7.837993	-4.880069
92	6	0	-2.022329	-9.487705	-4.718812

93	6	0	-1.331922	-8.267191	-4.128935
94	1	0	-2.802135	-9.849718	-4.038801
95	1	0	-2.503751	-9.245336	-5.670747
96	1	0	-2.057972	-7.485202	-3.883845
97	1	0	-0.653325	-7.837993	-4.880069

E(RB+HF-VWN+P86) = -1968.53088065 A.U.